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Supporting Information

Influence of Catalyst Structure and Reaction Conditions on *anti*- versus *syn*-Aminopalladation Pathways in Pd-Catalyzed Alkene Carboamination Reactions of *N*-Allylsulfamides

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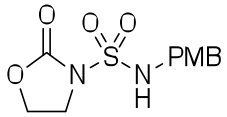
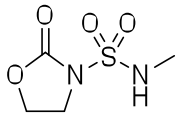
General: All reactions were carried out under a nitrogen atmosphere in flame-dried glassware unless otherwise noted. All reagents were obtained from commercial sources and were used as obtained unless otherwise noted. *N*-Benzyl-2-oxooxazolidine-3-sulfonamide,[1] *N*-(4-methoxyphenyl)-2-oxooxazolidine-3-sulfonamide,[1] *N*-benzylcyclopent-2-enylamine,[2] *N*-benzylbut-3-en-2-ylamine,[3] *N*-benzylallylamine,[4] *N*-benzylmethallylamine,[5] 1-allyl-1,3-bis-benzylsulfamide (**1a**),[1] 1-allyl-1-benzyl-3-(4-methoxyphenyl)sulfamide (**1f**),[1] 1,3-bis-benzyl-1-cyclopent-2-enylsulfamide (**12**),[1] (*Z*)-1-(3-*d*-allyl)-1-methyl-3-(4-nitrophenyl)urea (**20**),[6] 1-benzyl-

5-chloro-1*H*-indole,[7] 4-cyanophenyl triflate,[8] 4-chlorophenyl triflate,[8] 4-methoxyphenyl triflate,[8] 3-trifluromethylphenyl triflate,[9] 2-methylphenyl triflate,[10] and 3,4-methylenedioxyphenyl triflate[11] were prepared according to published procedures. Bulk quantities of lithium *tert*-butoxide and sodium *tert*-butoxide were stored in a glove box and removed in small amounts (ca. 1–2 g) that were consumed within a few days. Toluene, THF, diethyl ether and dichloromethane were purified using a GlassContour solvent purification system.

Preparation and Characterization of *N*-Allylsulfamide Substrate Precursors

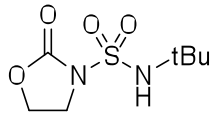


***N*-(4-Methoxybenzyl)-2-oxooxazolidine-3-sulfonamide (S1a).** The title compound was prepared from chlorosulfonyl isocyanate (0.87 mL, 10 mmol), 2-chloroethanol (0.67 mL, 10 mmol), and *p*-methoxybenzylamine (1.5 mL, 11 mmol), according to a procedure analogous to that described by Stahl.[1] This procedure afforded 1.56 g (54%) of the title compound as a white solid: mp = 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 9.0 Hz, 2 H), 6.88 (d, J = 8.6 Hz, 2 H), 5.64 (t, J = 6.2 Hz, 1 H), 4.25–4.19 (m, 4 H), 3.83 (dd, J = 7.1, 8.7 Hz, 2 H), 3.79 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 153.2, 129.6, 127.3, 114.2, 62.5, 55.4, 47.6, 44.8; IR (film) 3291, 1748, 1360, 1149 cm^{-1}. MS (ESI) 309.0511 (309.0516 calcd for $C_{11}H_{14}N_2O_5S$, M + Na^+).

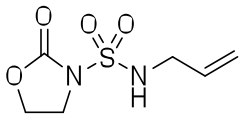


***N*-Methyl-2-oxooxazolidine-3-sulfonamide (S1b).** The title compound was prepared from chlorosulfonyl isocyanate (3.5 mL, 40 mmol), 2-chloroethanol (2.7 mL, 40 mmol) and methylamine (7.5 mL, 60 mmol, 8 M solution in ethanol), according to a procedure analogous to that described by Stahl except the workup was modified such that triethylamine hydrochloride was removed by column chromatography.[1] This procedure afforded 5.24 g (73%) of the title compound as a white solid: mp = 103–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (s, 1 H), 4.48 (dd, J = 7.1, 8.6 Hz, 2 H), 4.09 (dd, J = 7.1, 8.6 Hz, 2 H), 2.83 (d, J = 5.2 Hz, 3 H); ^{13}C NMR

(126 MHz, $CDCl_3$) δ 153.5, 62.6, 45.2, 30.0; IR (film) 3328, 1750, 1354, 1153 cm^{-1}. MS (ESI) 203.0098 (203.0097 calcd for $C_4H_8N_2O_4S$, M + Na^+).



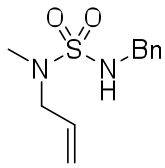
***N*-(*tert*-Butyl)-2-oxooxazolidine-3-sulfonamide (S1c).** The title compound was prepared from chlorosulfonyl isocyanate (3.5 mL, 40 mmol), 2-chloroethanol (2.7 mL, 40 mmol), and *tert*-butylamine (4.6 mL, 44 mmol) according to a procedure analogous to that described by Stahl.[1] This procedure afforded 7.21 g (81%) of the title compound as a white solid: mp = 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1 H), 4.40 (dd, *J* = 7.1, 8.7 Hz, 2 H), 4.04 (dd, *J* = 7.1, 8.7 Hz, 2 H), 1.35 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 62.4, 55.7, 44.5, 29.4; IR (film) 3250, 1756, 1362, 1145 cm^{-1}. MS (ESI) 245.0574 (245.0566 calcd for $C_7H_{14}N_2O_4S$, M + Na^+).



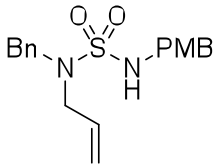
***N*-Allyl-2-oxooxazolidine-3-sulfonamide (S1d).** The title compound was prepared from chlorosulfonyl isocyanate (5.2 mL, 60 mmol), 2-chloroethanol (4.0 mL, 60 mmol), and allylamine (5.0 mL, 66 mmol) according to a procedure analogous to that described by Stahl except the workup was modified such that triethylamine hydrochloride was removed by column chromatography.[1] This procedure afforded 7.5 g (61%) of the title compound as a white solid: mp = 83–85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 6.0, 10.2, 17.0 Hz, 1 H), 5.57–5.46 (m, H), 5.40–5.23 (m, 2 H), 4.45 (dd, *J* = 6.6, 9.1 Hz, 2 H), 4.07 (dd, *J* = 6.6, 9.3 Hz, 2 H), 3.78 (tt, *J* = 1.4, 6.2 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 132.4, 118.6, 62.6, 46.5, 45.2; IR (film) 3286, 1747, 1356, 1146 cm^{-1}. MS (ESI) 229.0257 (229.0253 calcd for $C_6H_{10}N_2O_4S$, M + Na^+).

General Procedure A: Synthesis of *N*-Allyl Sulfamides

A flame dried flask was charged with the appropriate oxazolidinone substrate **S1** (1.0 equiv), 4-dimethylaminopyridine (0.2 equiv), and a stirbar, then was evacuated and backfilled with N_2. Acetonitrile was added, followed by Et_3N (3.0 equiv), and then the reaction vessel was placed in an oil bath at 80 °C and stirred for 30 minutes. The appropriate amine (1.1 equiv) was added and the resulting mixture was heated to reflux overnight (approximately 16 hours). The mixture was cooled to rt, solvent was removed via rotary evaporation, and the residue was partitioned between CH_2Cl_2 and 1 M HCl. The aqueous layer was extracted with CH_2Cl_2, the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography on silica gel.

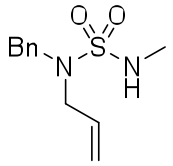


1-Allyl-3-benzyl-1-methylsulfamide (1b). The title compound was prepared from *N*-benzyl-2-oxooxazolidine-3-sulfonamide (1.9 g, 7.42 mmol) and *N*-allylmethylamine (0.78 mL, 8.16 mmol) according to general procedure A except the reaction temperature was lowered to 60 °C prior to addition of the amine. This procedure afforded 1.41 g (79%) of the title compound as a white solid: mp = 32–34 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5 H), 5.77 (ddt, *J* = 6.3, 10.1, 16.6 Hz, 1 H), 5.30–5.15 (m, 2 H), 4.45–4.31 (m, 1 H), 4.19 (d, *J* = 6.0 Hz, 2 H), 3.71 (d, *J* = 6.4 Hz, 2 H), 2.73 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 132.9, 128.7, 128.0, 127.9, 118.8, 53.2, 47.4, 34.3; IR (film) 3294, 1325, 1144 cm^{-1}. MS (ESI) 241.1010 (241.1005 calcd for $C_{11}H_{16}N_2O_2S$, M + H^+).

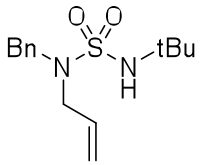


1-Allyl-1-benzyl-3-(4-methoxybenzyl)sulfamide (1c). The title compound was prepared from **S1a** (1.2 g, 4.2 mmol) and *N*-allylbenzylamine (0.72 mL, 4.62 mmol) according to general

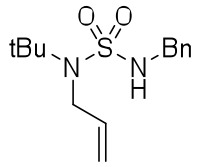
procedure A. This procedure afforded 1.18 g (81%) of the title compound as a white solid: mp = 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.1 Hz, 2 H), 5.83 (ddt, *J* = 6.5, 10.2, 16.8 Hz, 1 H), 5.25–5.13 (m, 2 H), 4.38 (s, 2 H), 4.17 (t, *J* = 6.0 Hz, 1 H), 4.10 (d, *J* = 5.9 Hz, 2 H), 3.79 (s, 3 H), 3.75 (d, *J* = 6.6 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 136.3, 132.8, 129.4, 128.7, 128.6, 128.6, 127.8, 119.5, 114.1, 55.3, 50.5, 49.9, 46.8; IR (film) 3286, 1243, 1145 cm^{-1}. MS (ESI) 369.1239 (369.1243 calcd for $C_{18}H_{22}N_2O_3S$, M + Na^+).



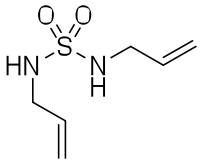
1-Allyl-1-benzyl-3-methylsulfamide (1d). The title compound was prepared from **S1b** (2.60 g, 14.4 mmol) and *N*-allylbenzylamine (2.49 mL, 15.9 mmol) according to general procedure A. This procedure afforded 2.91 g (84%) of the title compound as a clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5 H), 5.84 (ddt, *J* = 6.6, 10.2, 16.8 Hz, 1 H), 5.27–5.12 (m, 2 H), 4.36 (s, 2 H), 4.01 (s, 1 H), 3.72 (d, *J* = 6.7 Hz, 2 H), 2.67 (d, *J* = 5.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 132.7, 128.6, 128.5, 127.8, 119.5, 50.4, 49.7, 29.2; IR (film) 3311, 1312, 1144 cm^{-1}. MS (ESI) 263.0828 (263.0825 calcd for $C_{11}H_{16}N_2O_2S$, M + Na^+).



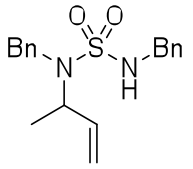
1-Allyl-1-benzyl-3-*tert*-butylsulfamide (1e). The title compound was prepared from **S1c** (2.22 g, 10 mmol) and *N*-allylbenzylamine (1.72 mL, 11 mmol) according to general procedure A. This procedure afforded 2.17 g (77%) of the title compound as a white solid: mp = 48–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5 H), 5.86 (ddt, *J* = 6.6, 10.1, 16.9 Hz, 1 H), 5.26–5.07 (m, 2 H), 4.35 (s, 2 H), 3.83 (s, 1 H), 3.71 (d, *J* = 6.8 Hz, 2 H), 1.33 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 132.9, 128.8, 128.5, 127.7, 119.3, 54.5, 50.4, 49.6, 30.0; IR (film) 3275, 1322, 1131 cm^{-1}. MS (ESI) 305.1295 (305.1294 calcd for $C_{14}H_{22}N_2O_2S$, M + Na^+).



1-Allyl-3-benzyl-1-*tert*-butylsulfamide (1g). The title compound was prepared from *N*-benzyl-2-oxooxazolidine-3-sulfonamide (2.56 g, 10 mmol) and *N*-allyl-*tert*-butylamine (1.64 mL, 11 mmol) according to general procedure A. This procedure afforded 2.06 g (73%) of the title compound as a white solid: mp = 75–76 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5 H), 5.99 (ddt, *J* = 5.9, 10.2, 17.2 Hz, 1 H), 5.29–5.12 (m, 2 H), 4.24 (t, *J* = 6.4 Hz, 1 H), 4.17 (d, *J* = 6.1 Hz, 2 H), 3.97 (dt, *J* = 1.5, 6.0 Hz, 2 H), 1.48 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 136.8, 128.7, 128.1, 127.9, 116.5, 59.2, 49.3, 47.3, 29.7; IR (film) 3327, 1317, 1135 cm^{-1}. MS (ESI) 305.1295 (305.1294 calcd for $C_{14}H_{22}N_2O_2S$, M + Na^+).

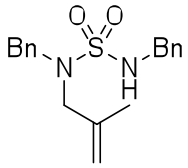


1,3-Bis-allylsulfamide (1h). The title compound was prepared from **S1d** (2.06 g, 10 mmol) and allylamine (1.5 mL, 20 mmol) according to general procedure A except the reaction temperature was lowered to 53 °C prior to addition of the amine. This procedure afforded 1.30 g (74%) of the title compound as a white solid: mp = 77–78 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (dddd, *J* = 5.6, 6.3, 10.4, 17.0 Hz, 2 H), 5.38–5.16 (m, 4 H), 4.31–4.13 (m, 2 H), 3.70 (tt, *J* = 1.5, 6.1 Hz, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.4, 117.7, 45.7; IR (film) 3277, 1312, 1146 cm^{-1}. MS (ESI) 177.0692 (177.0692 calcd for $C_6H_{12}N_2O_2S$, M + H^+).

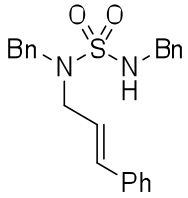


1,3-Bis-benzyl-1-but-3-en-2-ylsulfamide (7). The title compound was prepared from *N*-benzyl-2-oxooxazolidine-3-sulfonamide (3.51 g, 13.7 mmol) and *N*-benzylbut-3-en-2-ylamine (2.43 g,

15.1 mmol) according to general procedure A. This procedure afforded 2.90 g (64%) of the title compound as a white solid: mp = 46–48 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2 H), 7.37–7.25 (m, 6 H), 7.18 (dd, *J* = 1.7, 7.8 Hz, 2 H), 6.02 (ddd, *J* = 5.4, 10.6, 17.3 Hz, 1 H), 5.30–5.20 (m, 2 H), 4.55 (ddt, *J* = 1.7, 5.5, 7.1 Hz, 1 H), 4.38 (d, *J* = 15.5 Hz, 1 H), 4.26 (d, *J* = 15.6 Hz, 1 H), 4.07–3.96 (m, 3 H), 1.34 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 136.6, 128.7, 128.5, 128.2, 127.9, 127.8, 127.5, 117.1, 56.3, 48.1, 47.2, 17.7; IR (film) 3273, 1316, 1150 cm^{-1}. MS (ESI) 331.1479 (331.1475 calcd for $C_{18}H_{22}N_2O_2S$, M + H$^+$).

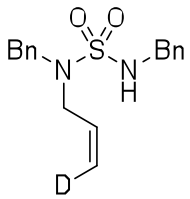


1,3-Bis-benzyl-1-methallylsulfamide (9). The title compound was prepared from *N*-benzyl-2-oxooxazolidine-3-sulfonamide (1.28 g, 5 mmol) and *N*-benzylmethallylamine (0.89 g, 5.5 mmol) according to general procedure A. This procedure afforded 1.29 g (78%) of the title compound as a white solid: mp = 59–60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 8 H), 7.26–7.23 (m, 2 H), 5.00 (s, 1 H), 4.95 (s, 1 H), 4.39 (s, 2 H), 4.21 (s, 1 H), 4.13 (s, 2 H), 3.77 (s, 2 H), 1.76 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 136.7, 136.3, 129.0, 128.7, 128.6, 127.9, 127.9, 127.9, 114.8, 53.5, 50.7, 47.3, 20.1; IR (film) 3289, 1317, 1132 cm^{-1}. MS (ESI) 331.1477 (331.1475 calcd for $C_{18}H_{22}N_2O_2S$, M + H$^+$).



1,3-Bis-benzyl-1-cinnamylsulfamide (11). The title compound was prepared from *N*-benzyl-2-oxooxazolidine-3-sulfonamide (1.03 g, 4.0 mmol) and *N*-benzylcinnamylamine (0.98 g, 4.4 mmol) according to general procedure A. This procedure afforded 1.01 g (64%) of the title compound as a white solid: mp = 87–90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.24 (m, 15 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 6.15 (dt, *J* = 6.9, 15.8 Hz, 1 H), 4.44 (s, 2 H), 4.36 (t, *J* = 6.2 Hz, 1 H), 4.23 (d, *J* = 6.0 Hz, 2 H), 3.93 (d, *J* = 7.0 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 136.3,

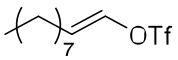
136.2, 134.6, 128.8, 128.7, 128.6, 128.6, 128.0, 128.0, 127.9, 126.5, 123.9, 50.7, 49.4, 47.3; IR (film) 3286, 1328, 1140 cm^{-1}. MS (ESI) 393.1635 (393.1631 calcd for $C_{23}H_{24}N_2O_2S$, M + H^+).



(*Z*)-1-(3-*d*-Allyl)-1,3-bis-benzylsulfamide (14). A flame dried round bottom flask equipped with a stirbar was cooled to rt under a stream of N_2 and charged with *N*-allylbenzylamine (10.0 mmol, 1.47 g) and Et_2O (20 mL). The resulting solution was cooled to –42 °C using a CO_2/CH_3CN bath and stirred for 5 min. A solution of *n*-BuLi in hexanes (7.5 mL, 1.6 M, 12 mmol) was added slowly and the resulting mixture was stirred at –42 °C for 20 min. A solution of *t*-BuLi in hexanes (13.75 mL, 1.6 M, 22 mmol) was added slowly and the resulting solution was stirred at –42 °C for 30 min. The CO_2/CH_3CN bath was replaced with a brine/ice bath and the reaction mixture was allowed to slowly warm to room temperature as the ice melted. The bath was removed and the mixture was stirred at rt for 1 h. The reaction mixture was then cooled to –78 °C and D_2O (3.6 mL, 200 mmol) from freshly cracked ampoules was slowly added. The resulting mixture was warmed to rt and stirred overnight. The reaction mixture was cooled to 0 °C, quenched with H_2O (15 mL) and transferred to a separatory funnel. The mixture was extracted with Et_2O (2 x 10 mL), the organic layers were combined and extracted with 1M HCl (3 x 10mL), and the organic layers were then discarded. The aqueous layers were combined, taken to pH 12 with 1M NaOH (40 mL), and extracted with CH_2Cl_2 (3 x 10mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to yield crude (*Z*)-N-(3-*d*-allyl)benzylamine.

A flame dried flask was then charged with 1-allyl-1,3-bis-benzylsulfamide (2.56 g, 10 mmol), 4-dimethylaminopyridine (244 mg, 2 mmol), and a stirbar, then was evacuated and backfilled with N_2. Acetonitrile (50mL) was added, followed by Et_3N (4.2 mL, 30 mmol), and then the reaction vessel was placed in an oil bath at 80 °C and stirred for 30 minutes. The crude amine was added and the resulting mixture was heated to reflux overnight (approximately 16 hours). The mixture was cooled to rt, solvent was removed via rotary evaporation, and the residue was partitioned between CH_2Cl_2 and 1 M HCl. The aqueous layer was extracted with CH_2Cl_2, the combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated in

vacuo. The resulting crude product was purified by flash chromatography on silica gel to yield 1.20 g (38%) of the title compound as an off-white solid, mp = 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 10 H), 5.80 (tdd, *J* = 2.4, 4.7, 9.0 Hz, 1 H), 5.21 (dt, *J* = 1.1, 10.2 Hz, 1 H), 4.38 (s, 2 H), 4.27 (t, *J* = 6.1 Hz, 1 H), 4.16 (d, *J* = 6.0 Hz, 2 H), 3.75 (d, *J* = 6.7 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 136.2, 132.6, 128.8, 128.6, 128.6, 128.0, 127.9, 127.8, 119.3 (t, *J* = 23.8 Hz), 50.6, 49.8, 47.3; IR (film) 3257, 1299, 1142 cm^{-1}. MS (ESI) 318.1387 (318.1381 calcd for $C_{17}H_{19}DN_2O_2S$, M + H$^+$).

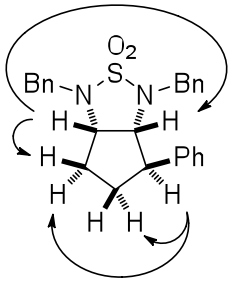


(*E*)-Dec-1-en-1-yl trifluoromethanesulfonate. The title compound was prepared from decanal (1.88 mL, 10 mmol), 2,6-di-*tert*-butylpyridine (2.65 mL, 12 mmol), and triflic anhydride (1.85 mL, 11 mmol) in DCE according to a procedure analogous to that described by Stang.[12] This procedure afforded 1.21 g (42%) of the title compound as a colorless oil. This compound was obtained as an 5:1 mixture of *E*:*Z* isomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56-6.46 (m, 1.2 H), 5.77 (dt, *J* = 7.7, 11.7 Hz, 0.2 H), 5.25 (td, *J* = 5.6, 7.6 Hz, 1.0 H), 2.19 (qd, *J* = 1.6, 7.5 Hz, 2.0 H), 2.04 (qd, *J* = 1.5, 7.5 Hz, 0.4 H), 1.40 (p, *J* = 7.1 Hz, 2.4 H), 1.36–1.20 (m, 12.0 H), 0.88 (t, *J* = 6.8 Hz, 3.6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 135.1, 122.9, 120.8, 118.6 (q, *J* = 320.7 Hz), 31.8, 29.2, 29.1, 29.0, 28.8, 28.6, 28.5, 26.5, 24.1, 22.6, 14.0; IR (film) 2926, 1422, 1204, 1142 cm^{-1}. MS (ESI) 287.0928 (287.0934 calcd for $C_{11}H_{19}F_3O_3S$, M + H$^-$).

Assignment of Stereochemistry

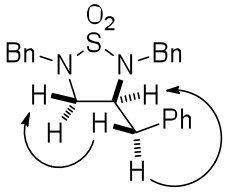
Sulfamide 13

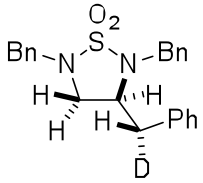
The stereochemistry of **13** was assigned on the basis of 1D NOESY experiments. The key nOe signals are shown below.

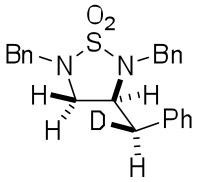


Sulfamides 15, 19

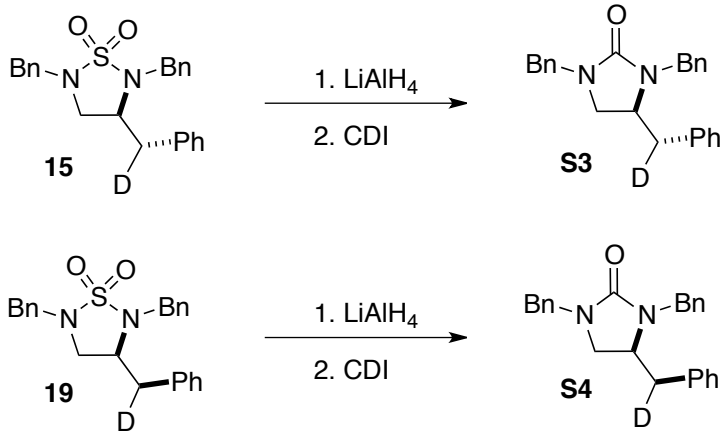
The stereochemistry of deuterated products **15** and **19** were assigned on the basis of 1D NOESY experiments carried out with the all-proteo analog of these compounds. The key nOe signals are shown below. The stereochemistry of the deuterated products was then assigned by examining which signal in each product was absent from the ^{1}H NMR spectrum.







To provide further support for the assignments of **15** and **19**, these compounds were converted to the corresponding ureas via reduction with $LiAlH_4$ and carbonylation with CDI. The proton NMR spectra of **S2** (the urea derived from **15**) was similar to that of **22,** whereas the proton NMR spectr of **S3** (the urea derived from **19**) was similar to that of **21**, with respect to the relative chemical shifts of the aliphatic protons and the coupling constants. Data for **S2** and **S3** are provided below.

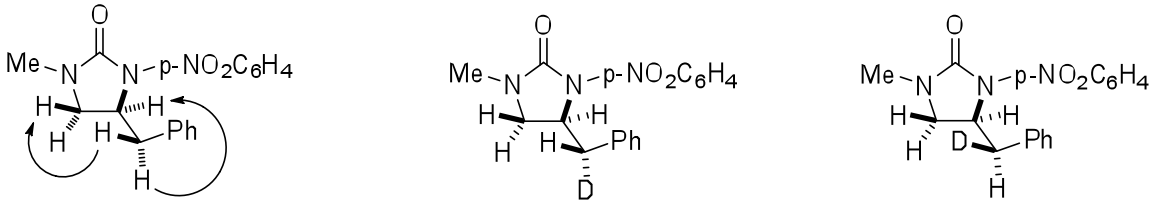


(±)-(1'*S*,3*S*)-2,3,5-Tribenzyl-1'-deuterioimidazolidin-2-one (S3). 75 mg (0.19 mmol) of **15** was cleaved with $LiAlH_4$ using a procedure similar to that of Chemler.[13] The crude product was dissolved in 1 mL THF and CDI (0.29 mmol, 47.0 mg) in 1 mL THF was added and brought to reflux for 24 h. Solvent was then removed and the product was purified by flash chromatography on silica gel to afford 34 mg (50%) of the title compound as a clear colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.40–7.14 (m, 13 H), 6.95 (d, *J* = 7.0 Hz, 2 H), 4.94 (d, *J* = 15.1 Hz, 1 H), 4.40 (d, *J* = 14.8 Hz, 1 H), 4.36 (d, *J* = 15.0 Hz, 1 H), 4.14 (d, *J* = 15.1 Hz, 1 H), 3.61–3.54 (m, 1 H), 3.05–2.99 (m, 2 H), 2.86 (dd, *J* = 6.9, 9.0 Hz, 1 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.7, 137.4, 137.2, 136.6, 129.0, 128.6, 128.6, 128.5, 128.2, 127.9, 127.4, 127.3, 126.7, 53.5, 48.1, 47.5, 46.0, 38.2 (t, *J* = 20.0 Hz); IR (film) 1685 cm^{-1}. MS (ESI) 358.2026 (358.2024 calcd for $C_{24}H_{23}DN_2O$, M + H^+).

(±)-(1'*R*,3*S*)-2,3,5-Tribenzyl-1'-deuterioimidazolidin-2-one (S4). 45 mg (0.11 mmol) of **19** was cleaved $LiAlH_4$ using a procedure similar to that of Chemler.[13] The crude product was dissolved in 1 mL THF and CDI (0.17 mmol, 27.6 mg) in 1 mL THF was added and brought to reflux for 24 h. Solvent was then removed and the product was purified by flash chromatography on silica gel to afford 28 mg (71%) of the title compound as a clear colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38–7.13 (m, 13 H), 6.95 (d, *J* = 7.1 Hz, 2 H), 4.93 (d, *J* = 15.1 Hz, 1 H), 4.39 (d, *J* = 15.0 Hz, 1 H), 4.36 (d, *J* = 15.0 Hz, 1 H), 4.13 (d, *J* = 15.3 Hz, 1 H), 3.60–3.53 (m, 1 H), 3.05–3.00 (m, 1 H), 2.86 (dd, *J* = 6.9, 8.9 Hz, 1 H), 2.56–2.46 (m, 1 H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.7, 137.3, 137.2, 136.6, 129.0, 128.6, 128.6, 128.5, 128.2, 127.9, 127.4, 127.3, 126.7, 53.5, 48.1, 47.5, 46.0, 38.3 (t, *J* = 20.0 Hz); IR (film) 1685 cm^{-1}. MS (ESI) 358.2026 (358.2024 calcd for $C_{24}H_{23}DN_2O$, M + H^+).

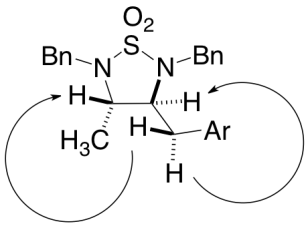
Ureas 21 and 22

The stereochemical assignment of urea **21** has been previously reported.[6] The stereochemistry of deuterated urea **22** was assigned on the basis of 1D NOESY experiments. The key nOe signals are shown below. The stereochemistry of the deuterated products was then assigned by examining which signal in each product was absent from the ^{1}H NMR spectrum.



Sulfamide 8

The stereochemistry of sulfamide **8** was assigned on the basis of 1D NOESY experiments. The key nOe signals are shown below.



Ar = *p*-CNC_6H_4

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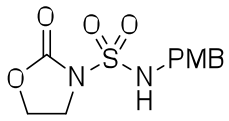
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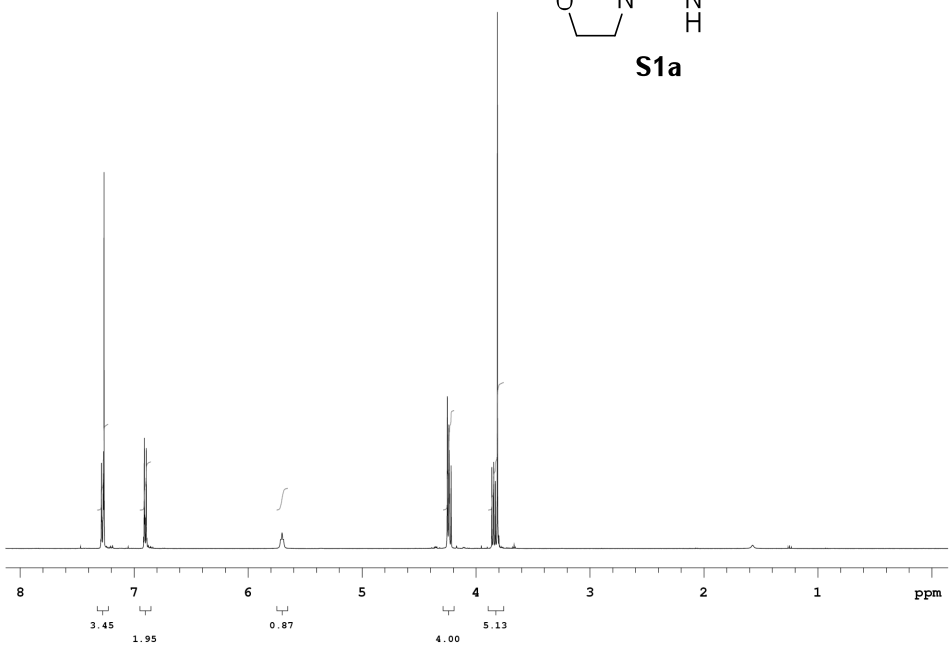
O
N
S
N
H
PMB

S1a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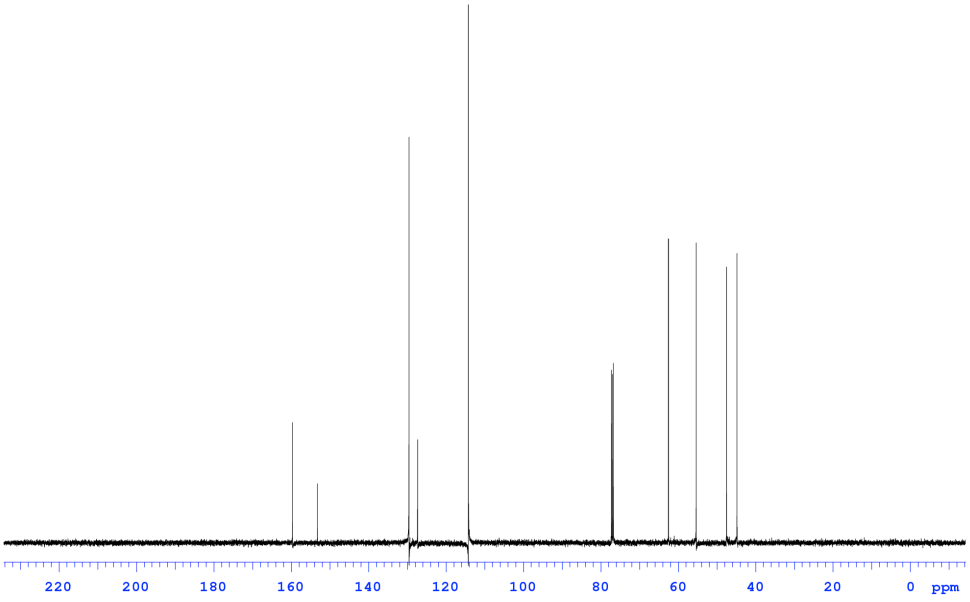
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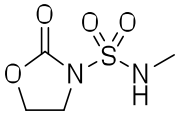
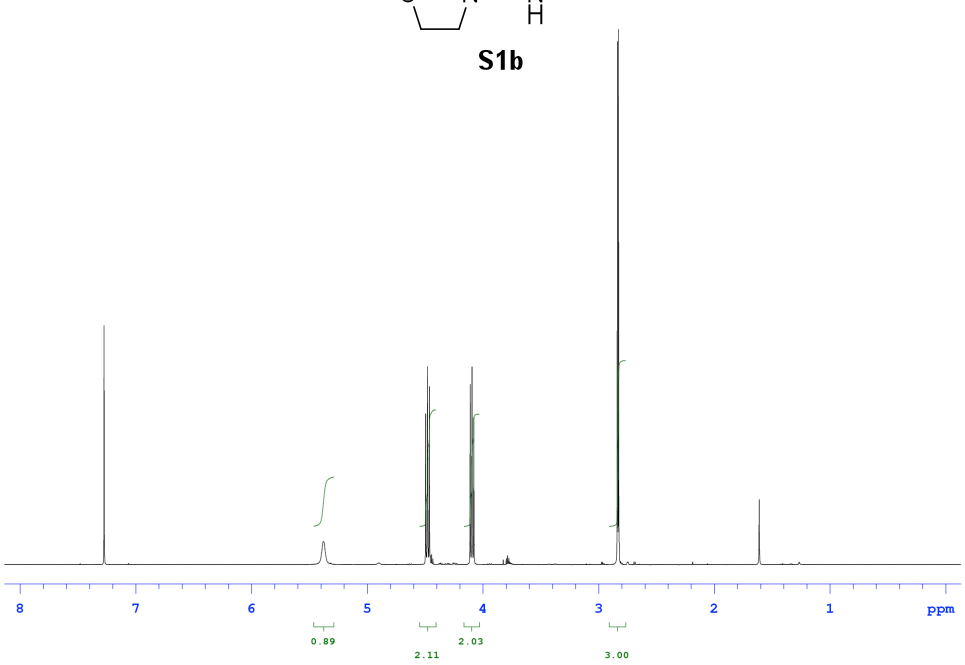


S1b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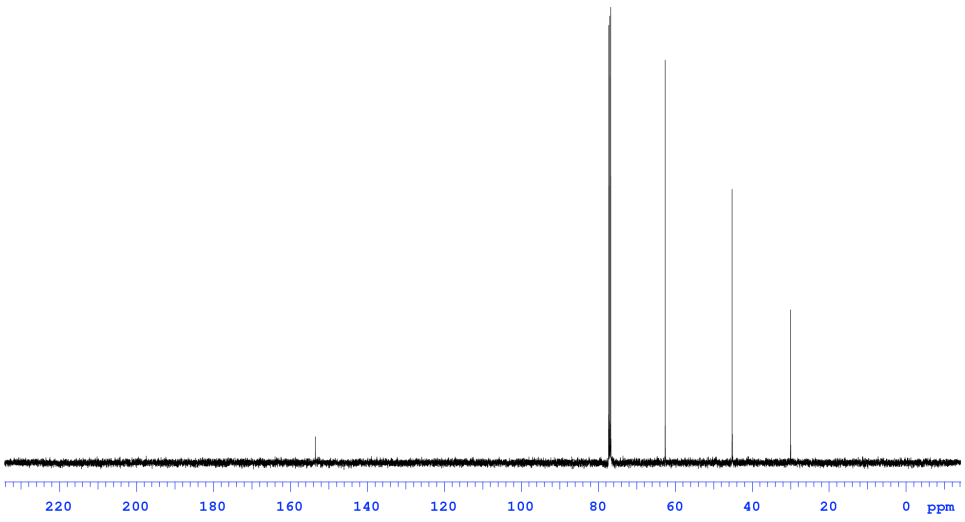
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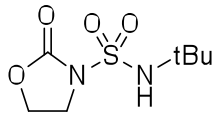
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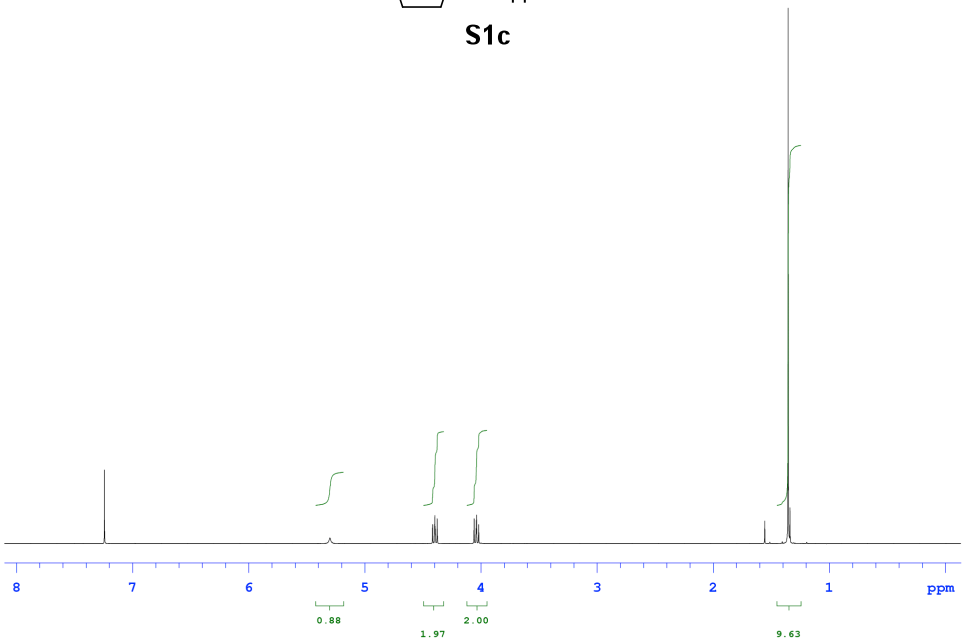
N
H
tBu

S1c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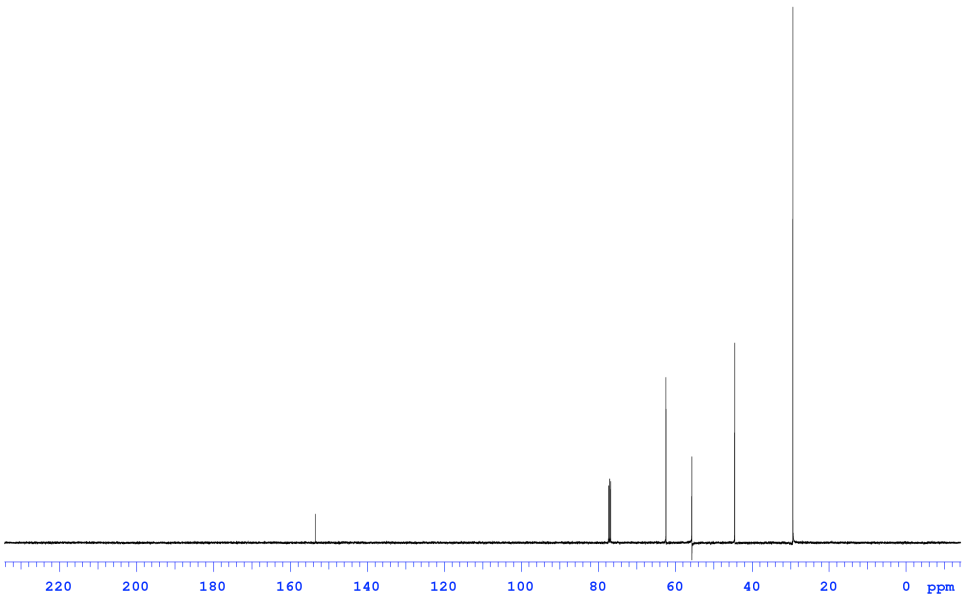
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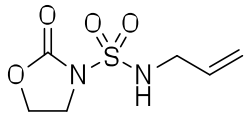

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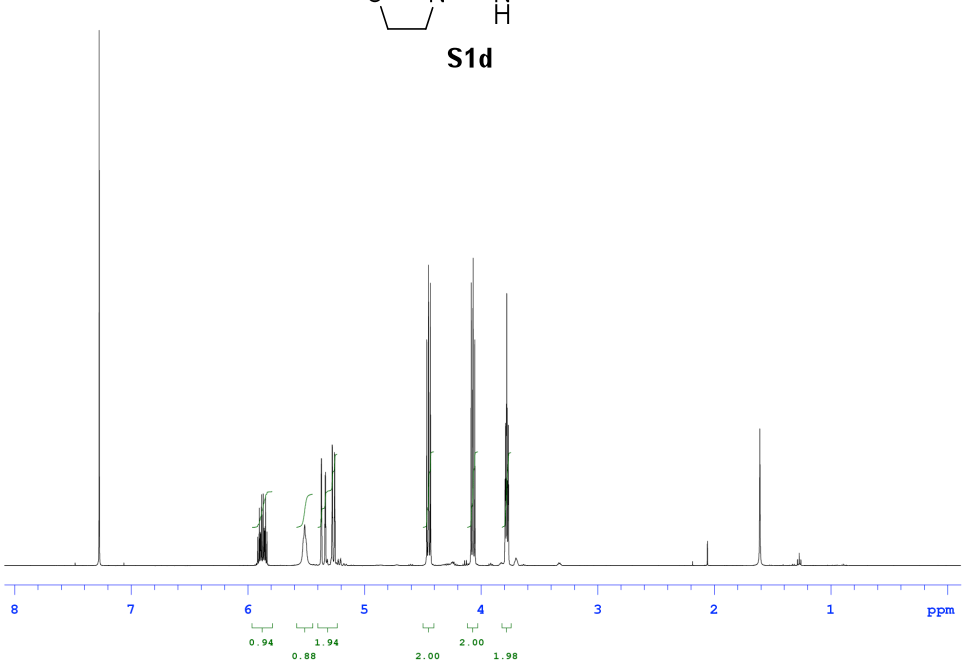
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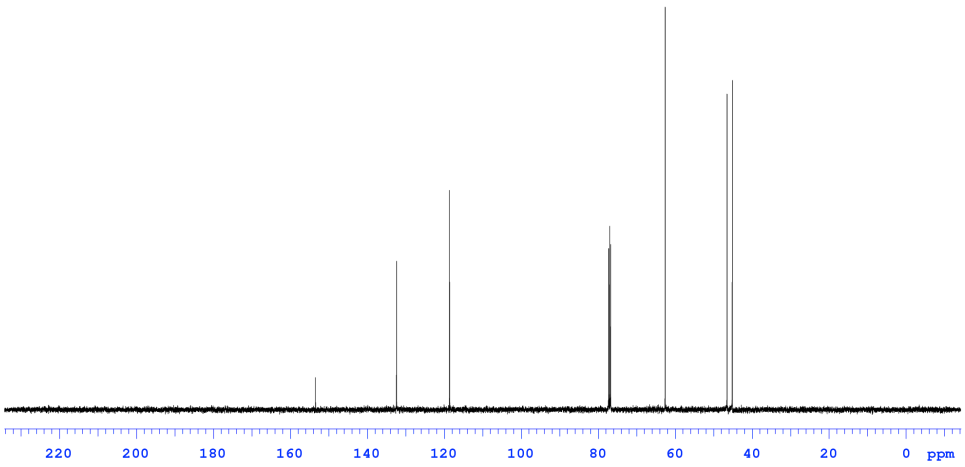
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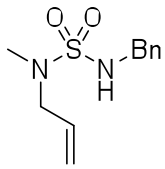
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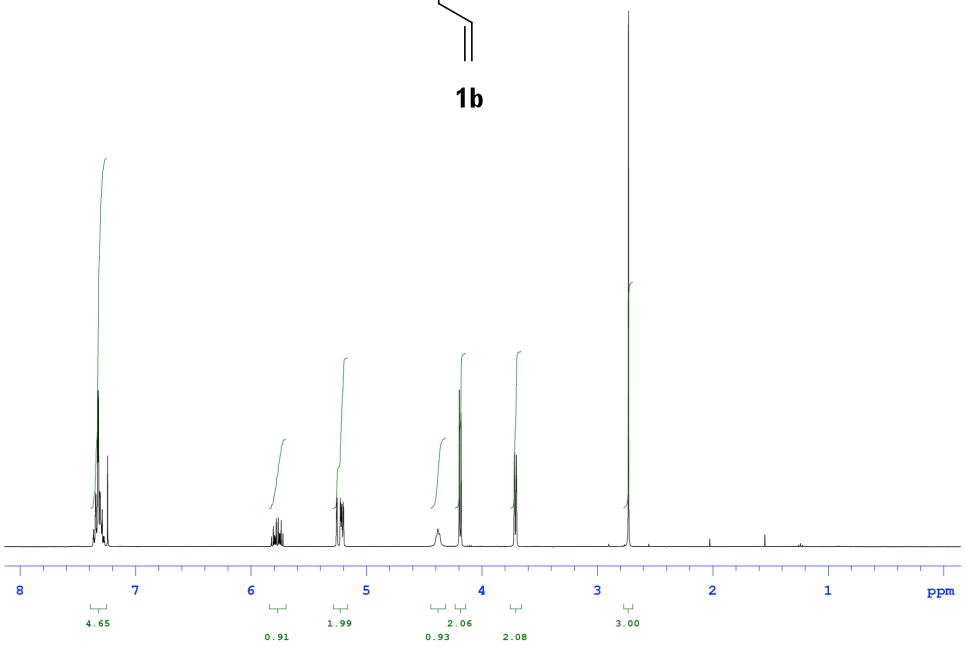
1b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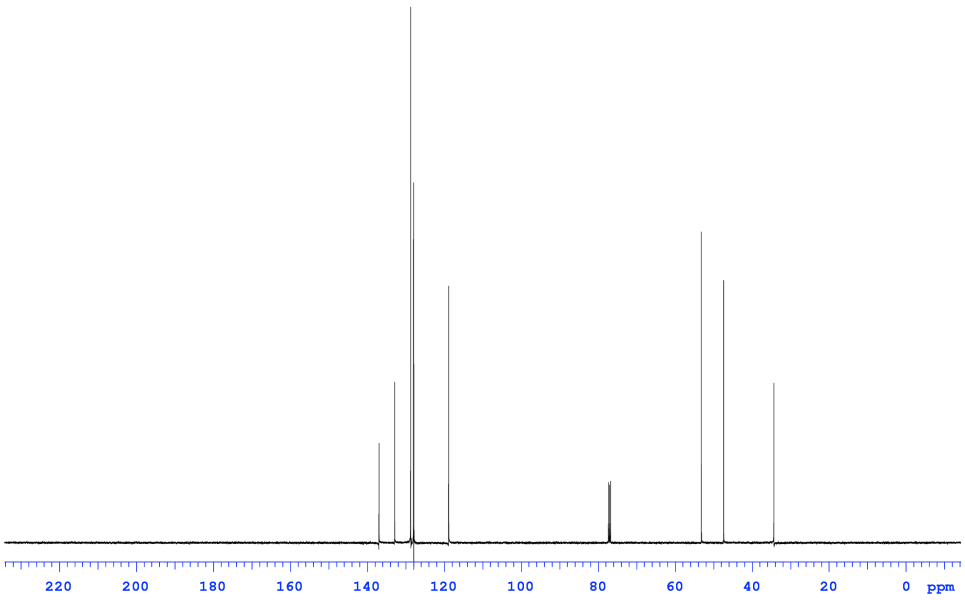
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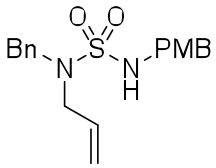
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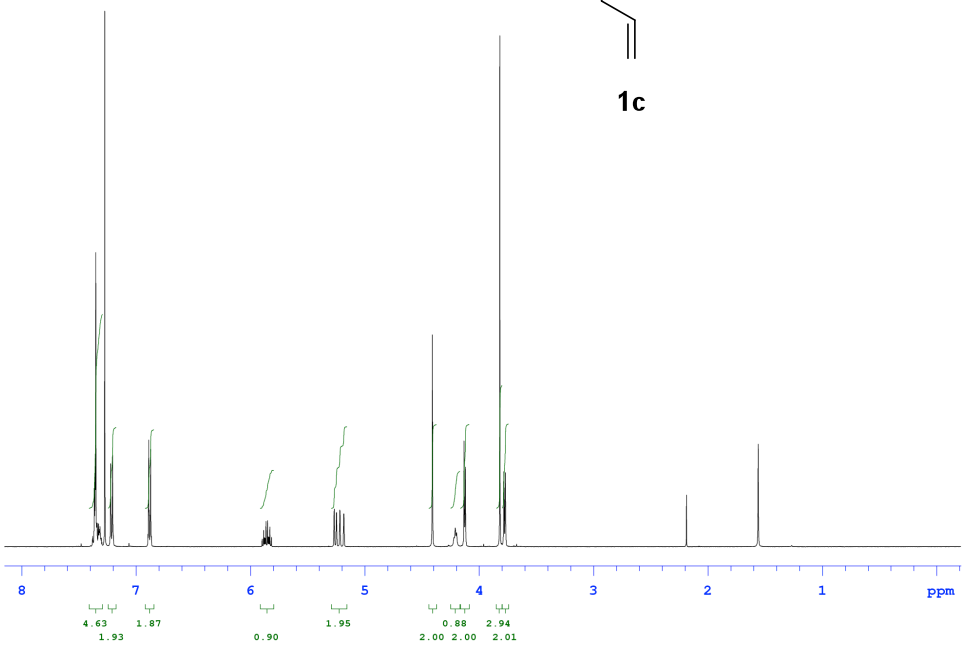
1c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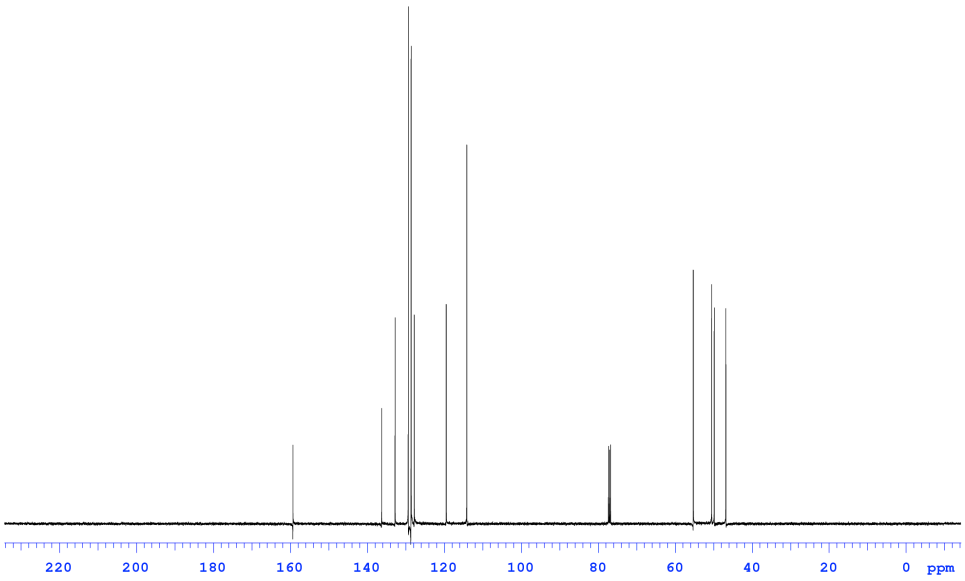
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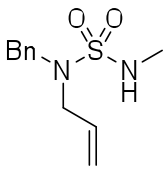
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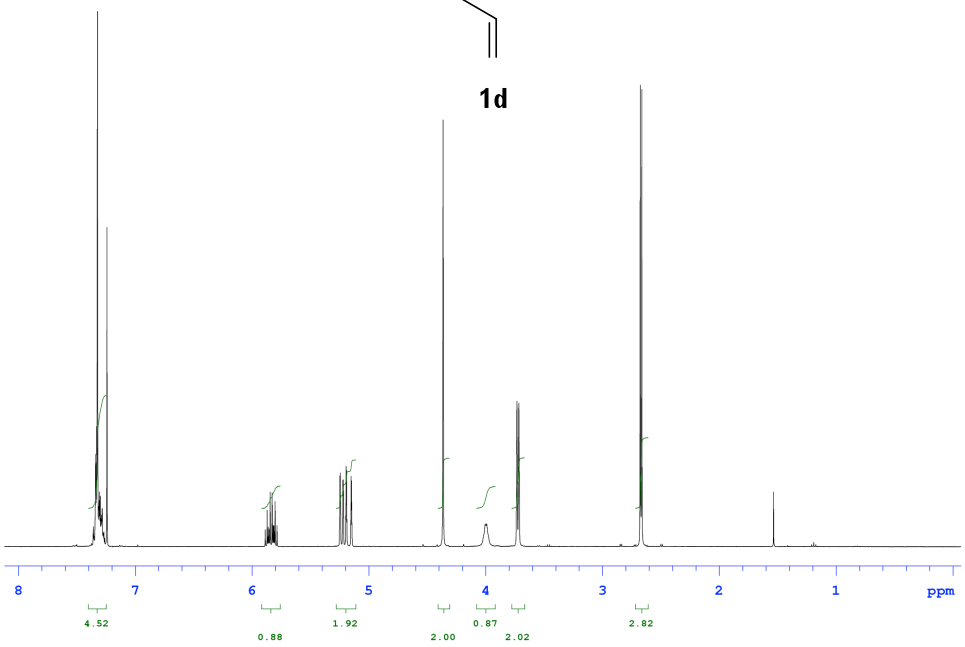
H

1d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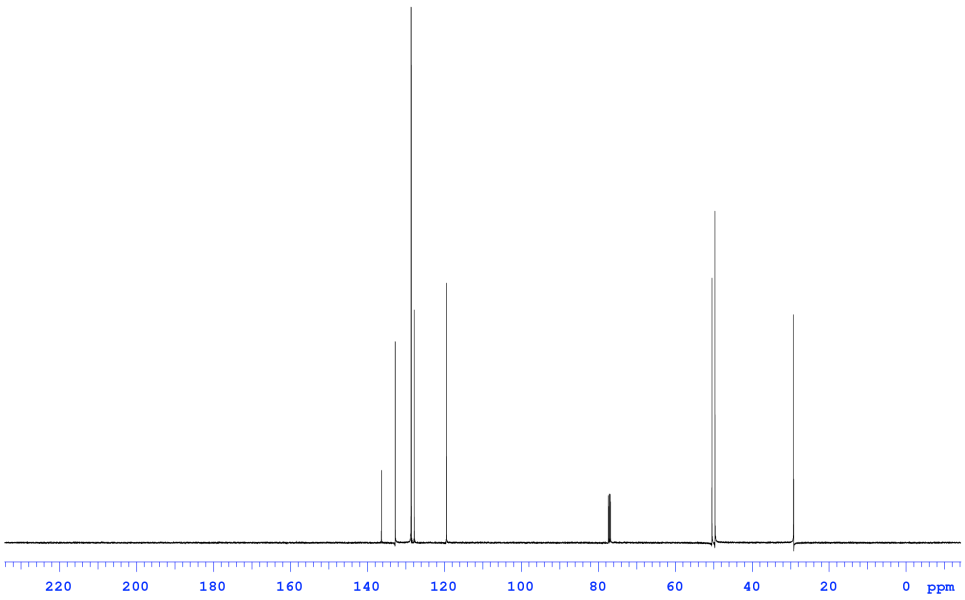
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140
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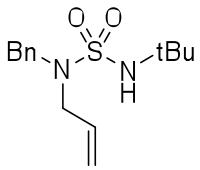
20
0
ppm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Bn
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S
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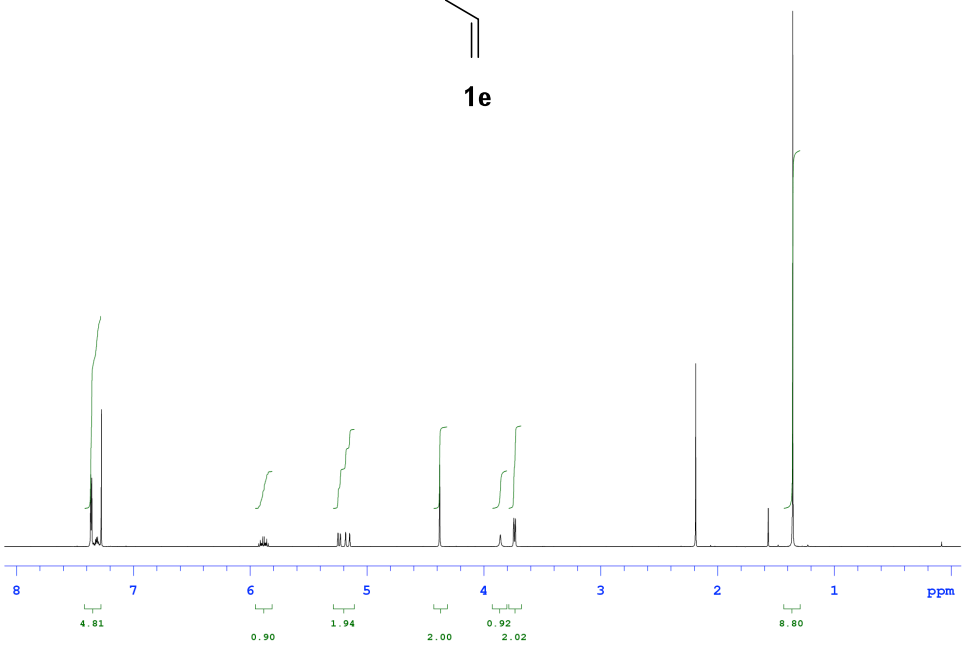
H
tBu

1e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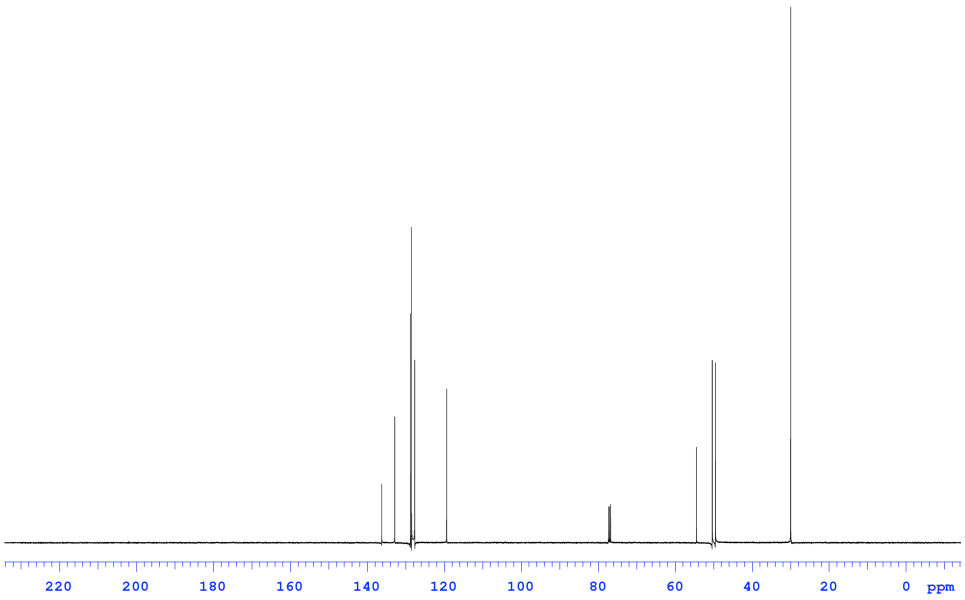
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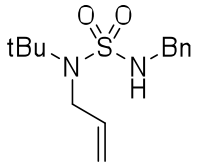
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Bn

1g

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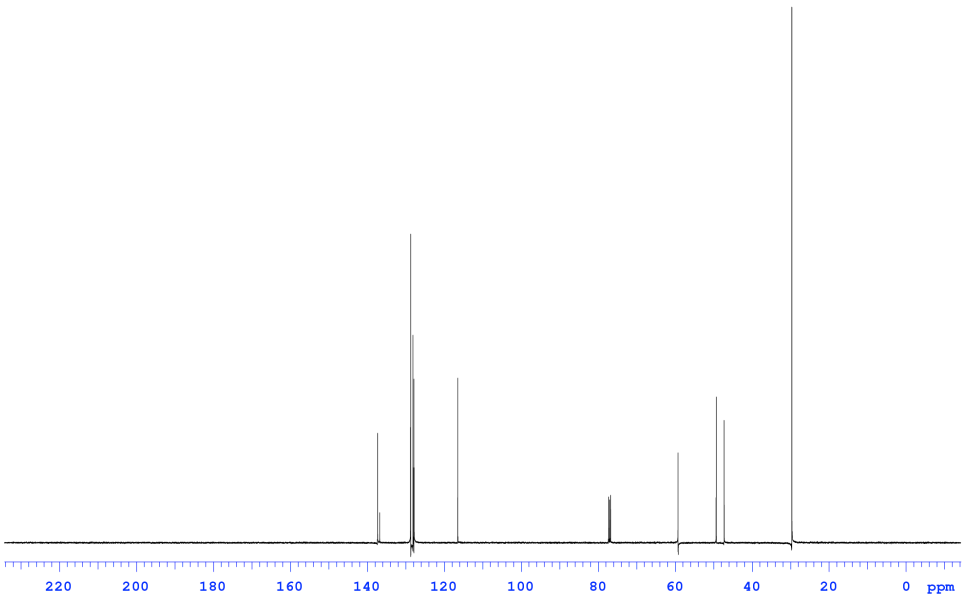
8.84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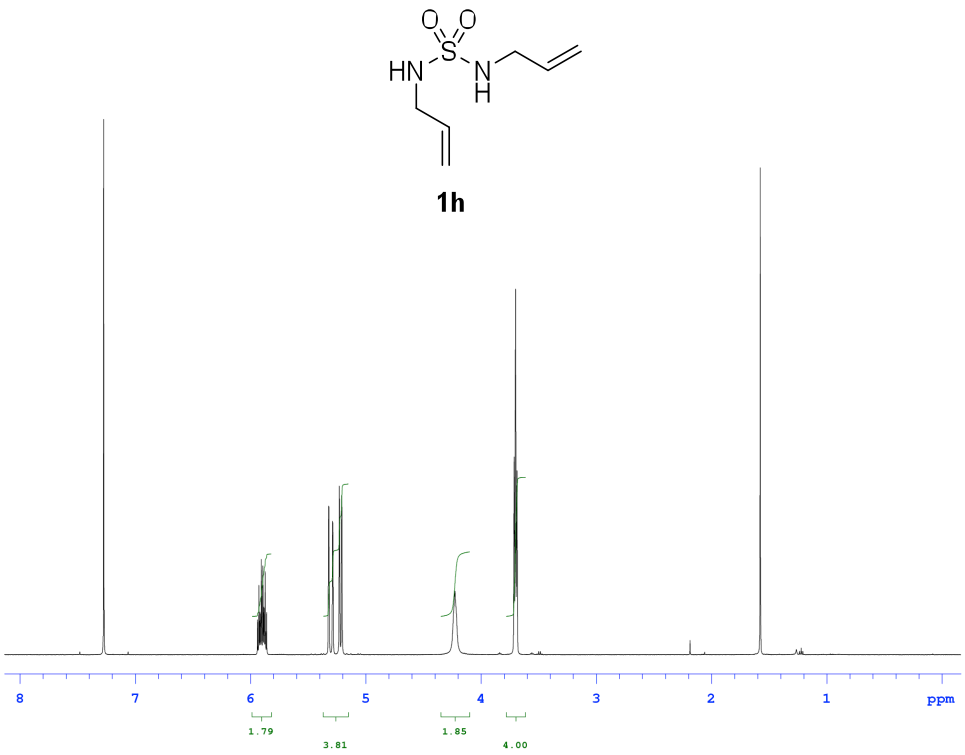
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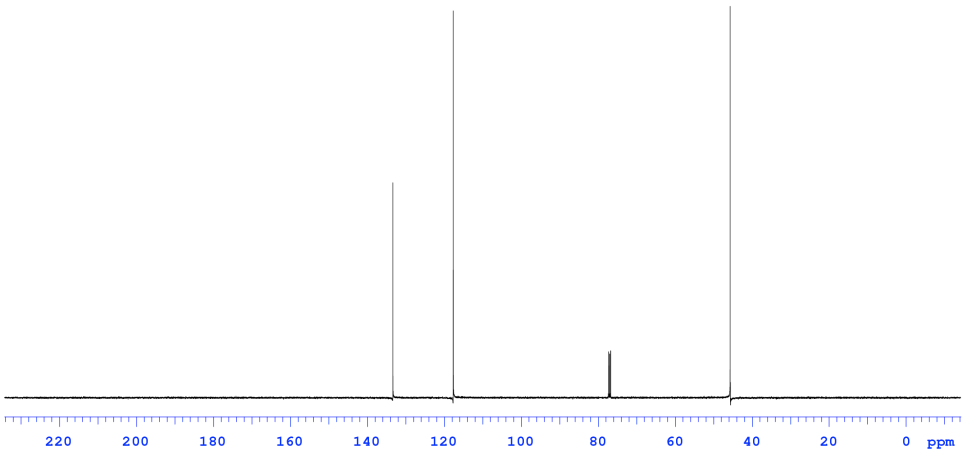
4.00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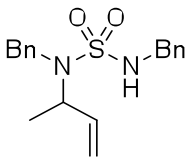
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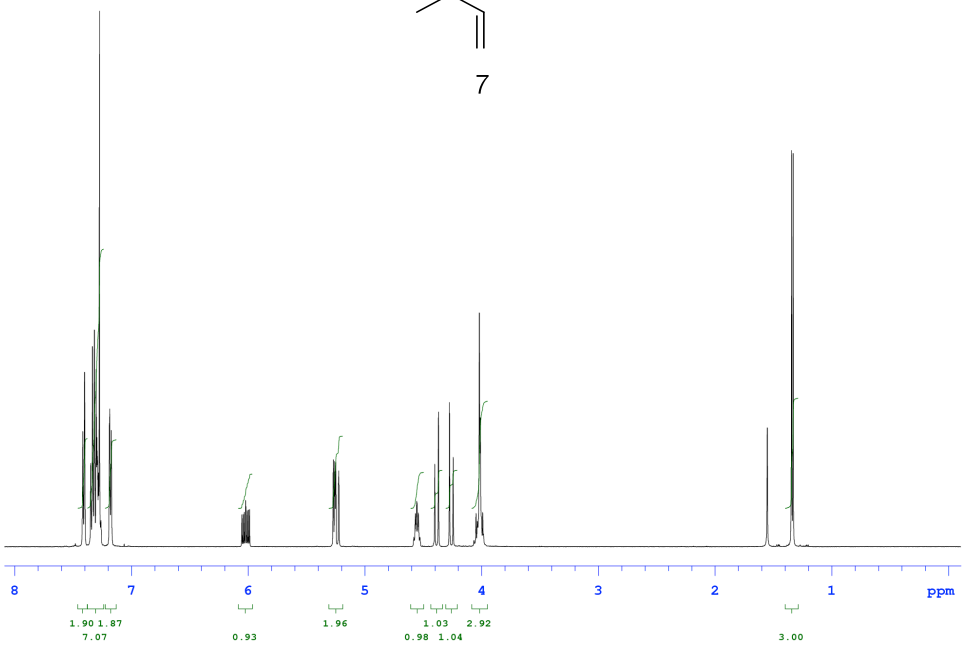
S
N
Bn
H

7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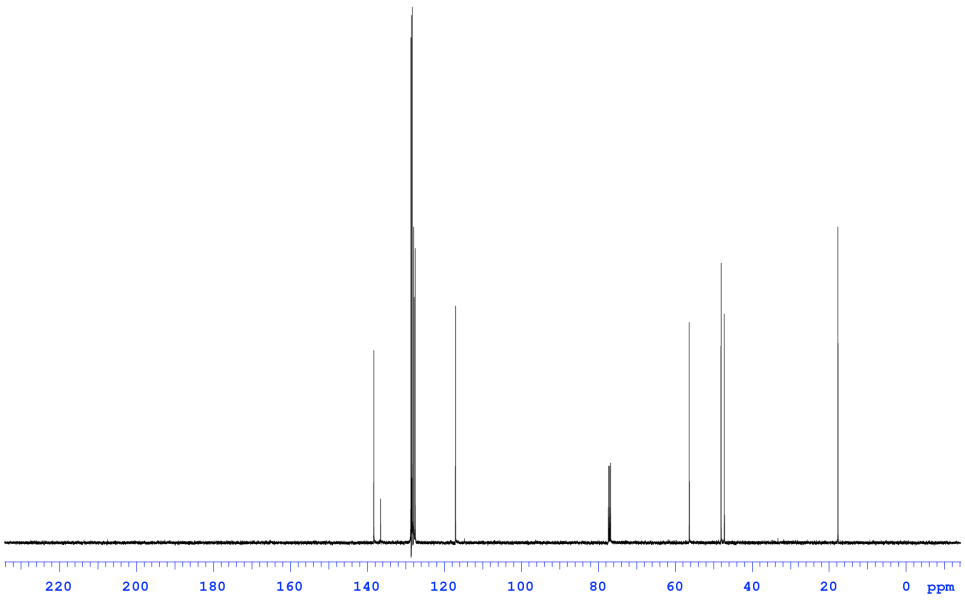
3.00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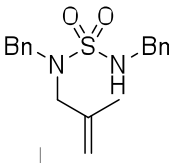
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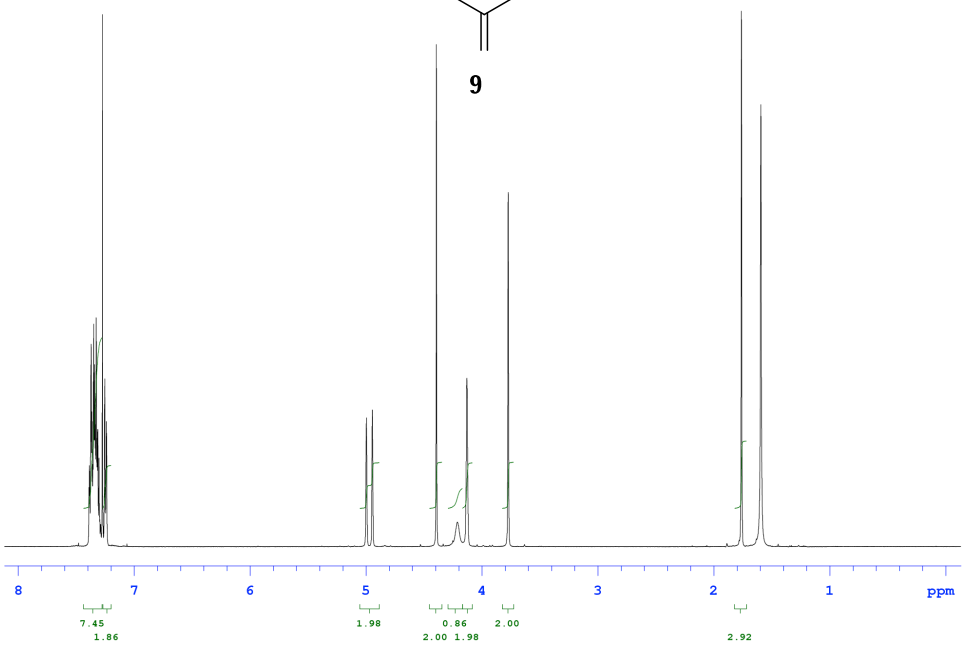
Bn
S
Bn
N
N
H

9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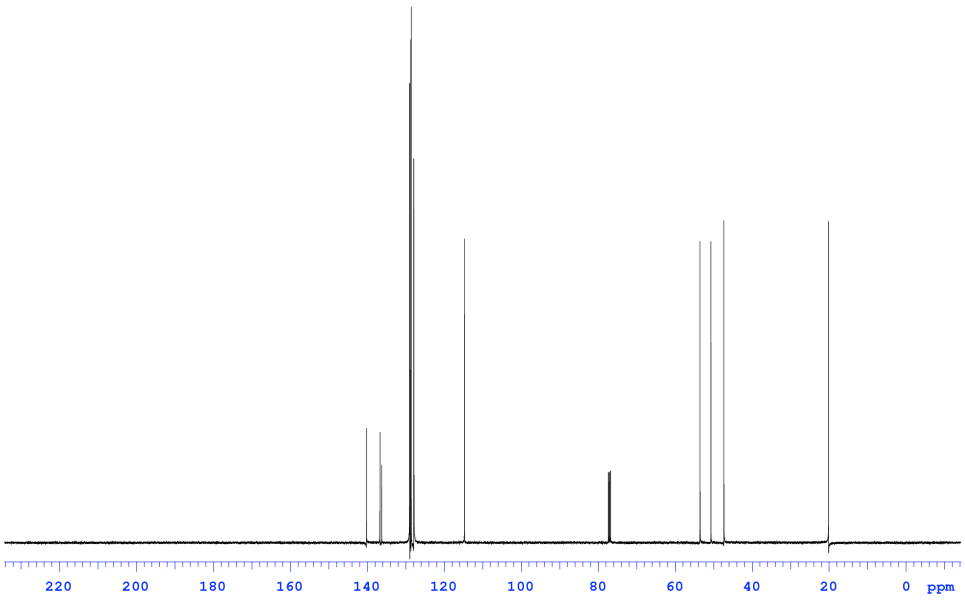
2.00
2.92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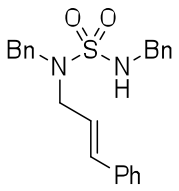
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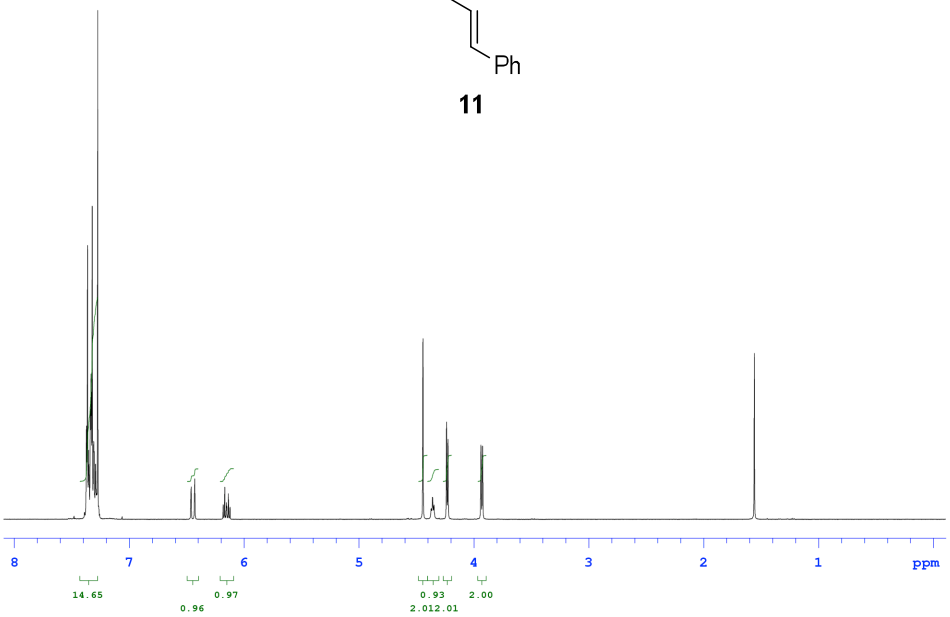
O
Bn
N
S
N
Bn
H
Ph

11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0.97
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2.012.01
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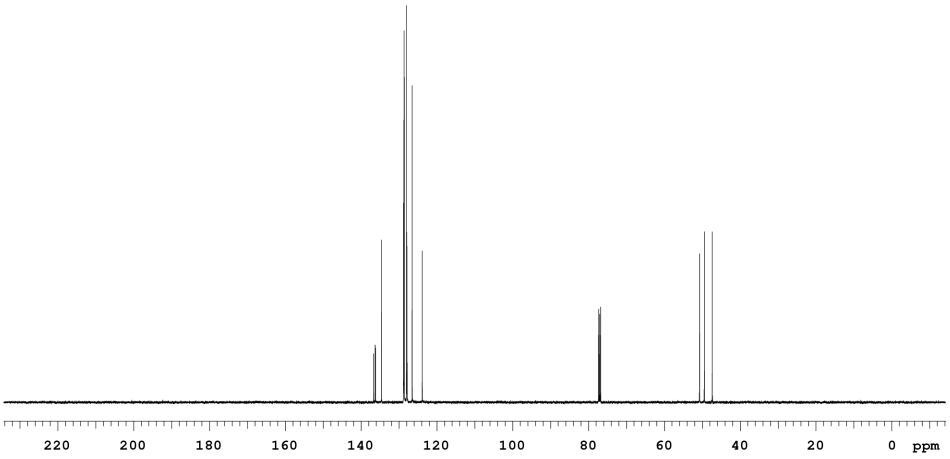
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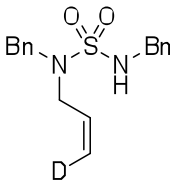
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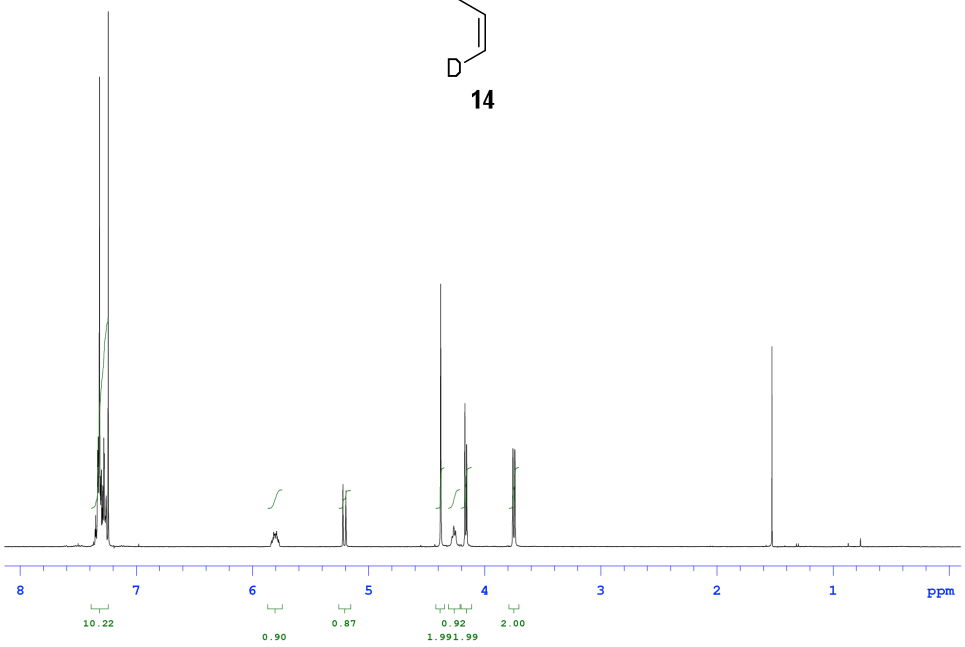
O
Bn
S
Bn
N
N
H
D

14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4
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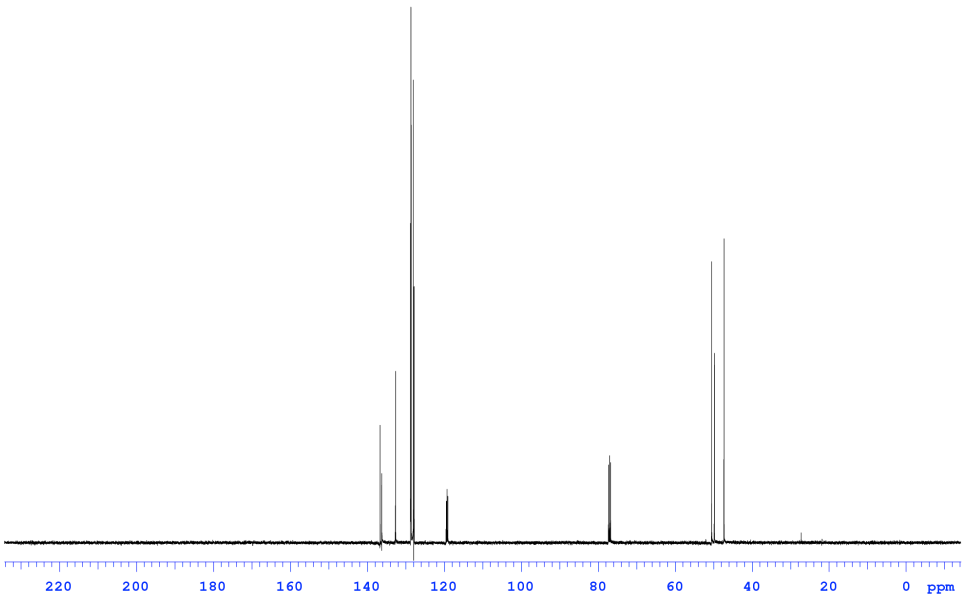
1.99
2.00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140
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100
80
60
40
20
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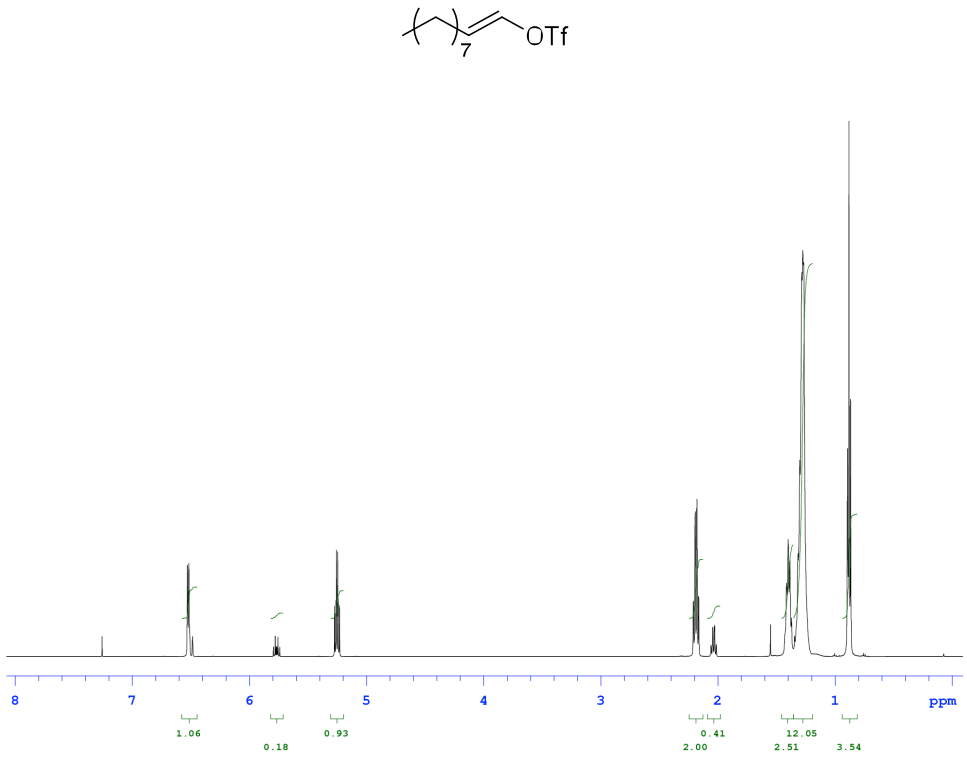
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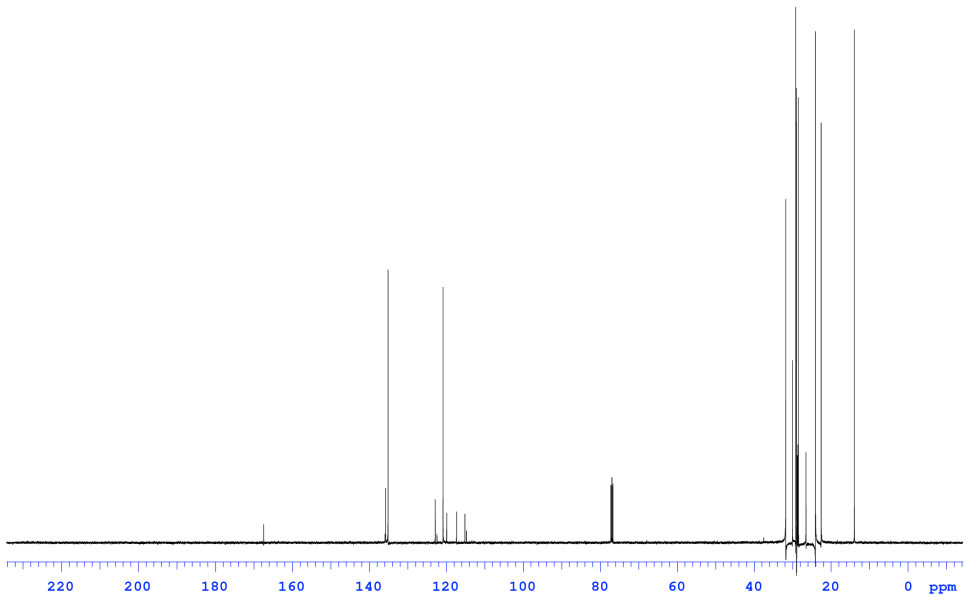
3.54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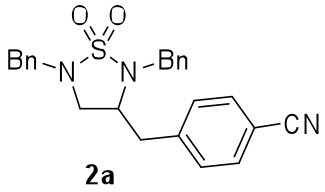
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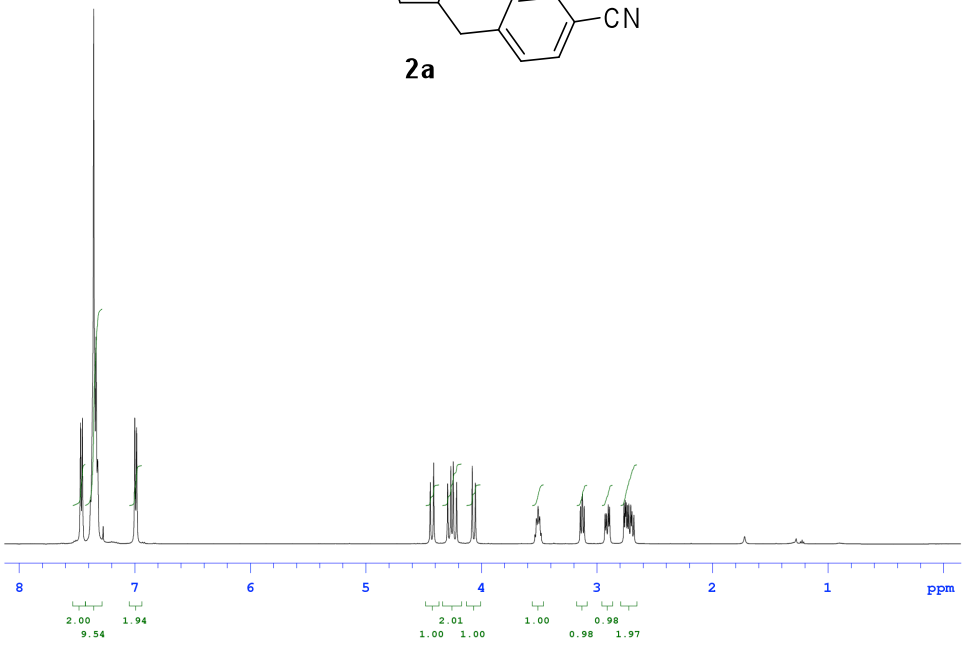
Bn
N
N
Bn
CN

2a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5
4
3
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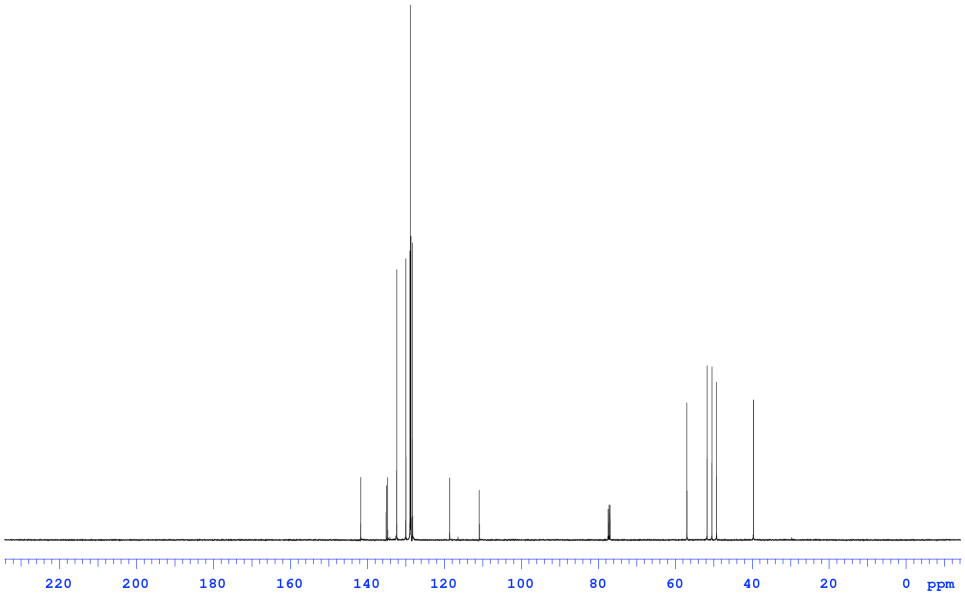
1.94
9.54
2.01
1.00
1.00
1.00
0.98
0.98
1.97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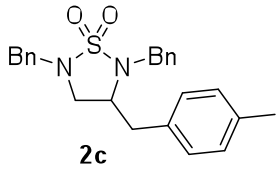
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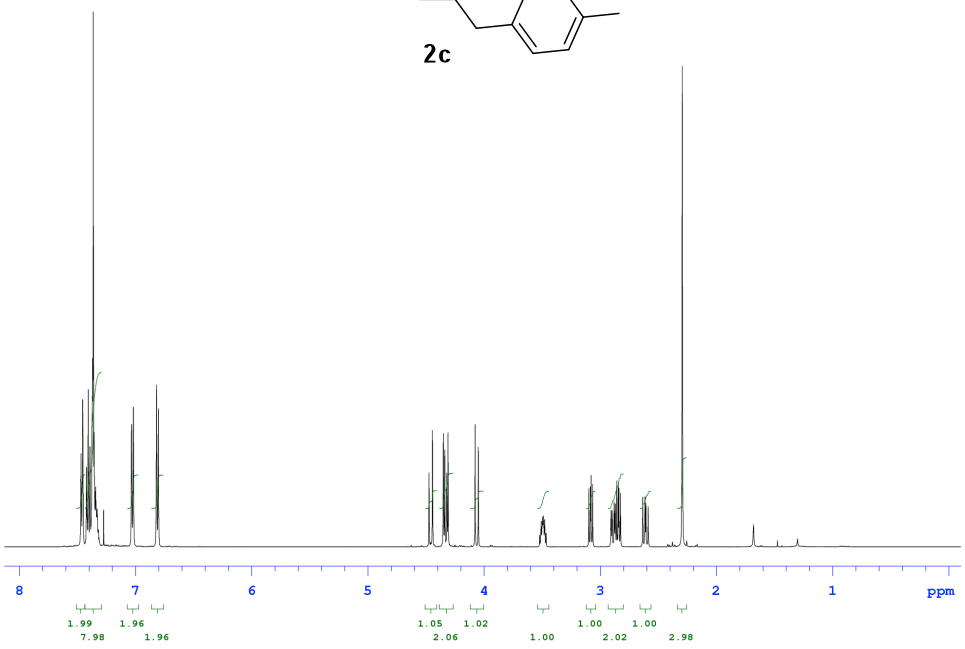
S
Bn
N
N
Bn

2c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6
5
4
3
2
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ppm
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1.96
1.05
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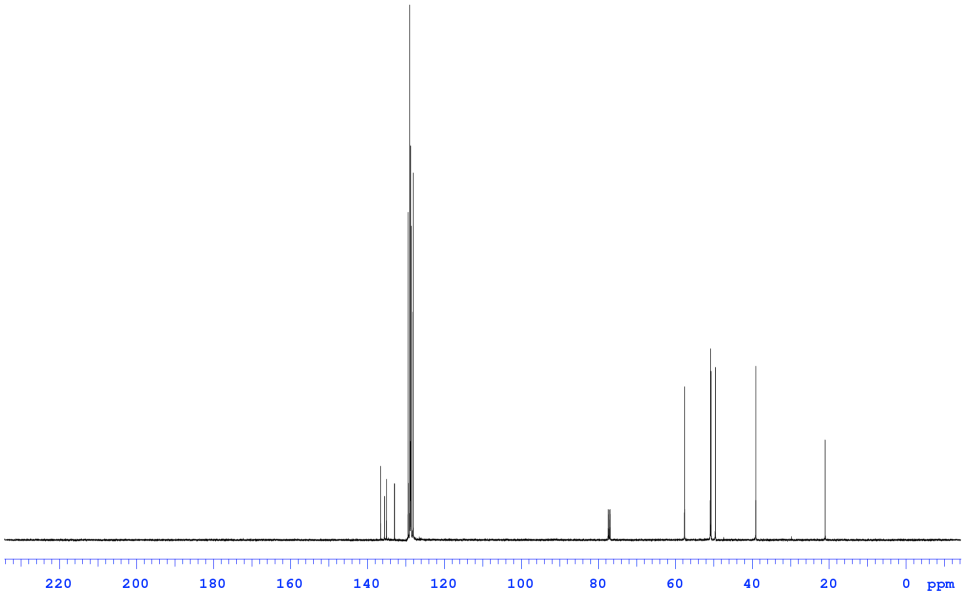
2.06
1.00
1.00
2.02
1.00
2.98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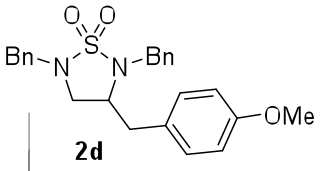
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Bn
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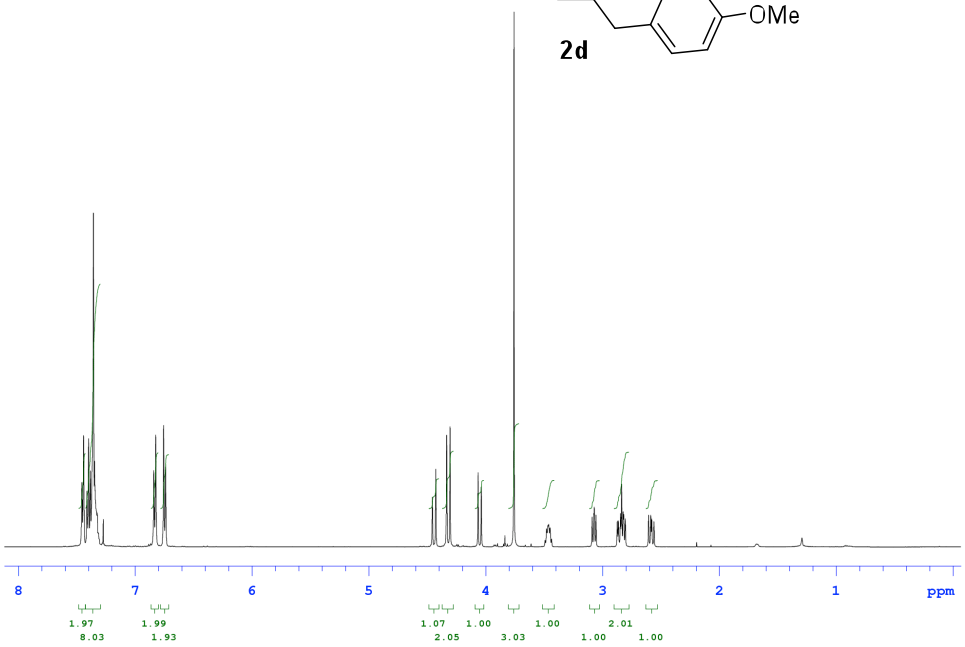
N
Bn
OMe

2d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4
3
2
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ppm
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1.07
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3.03
1.00
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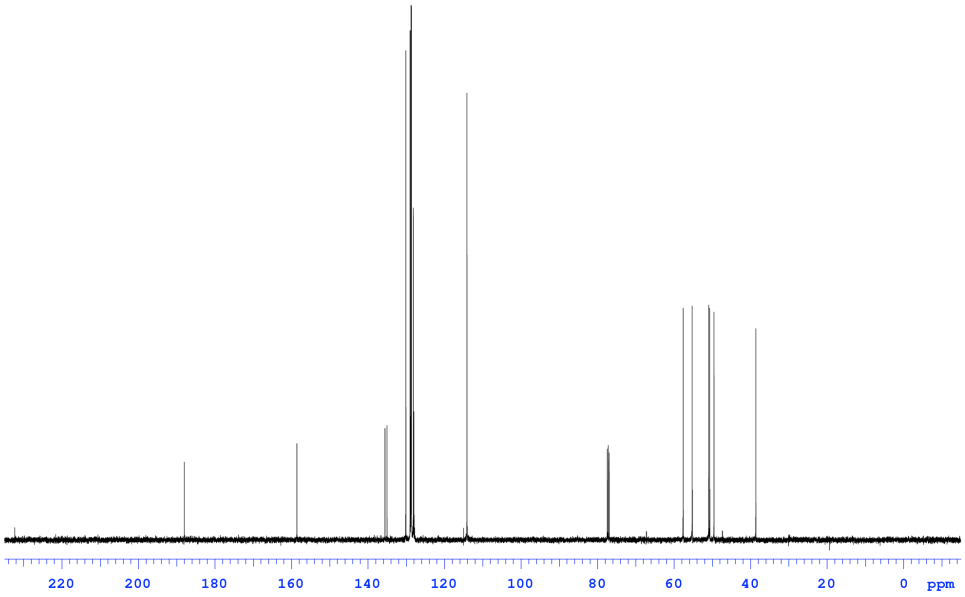
2.01
1.00
1.00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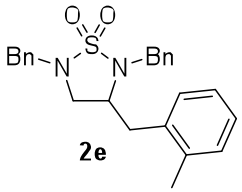
ppm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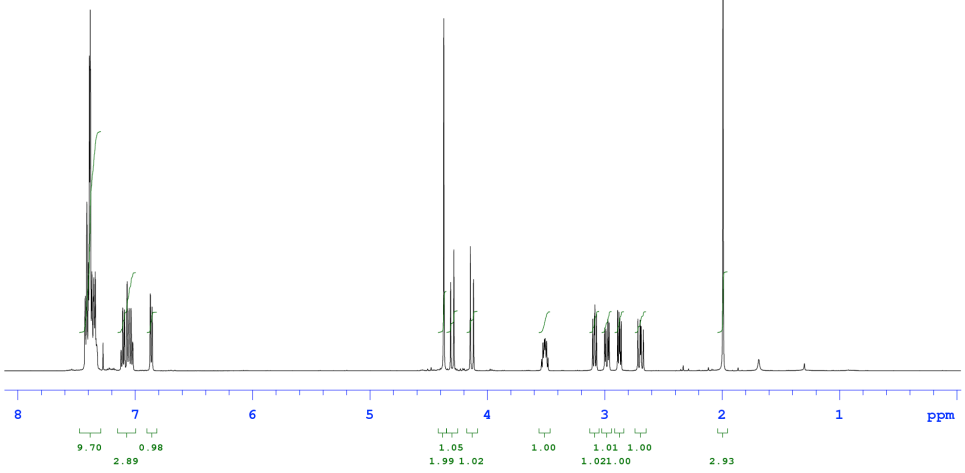
O
S
Bn
N
N
Bn

2e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4
3
2
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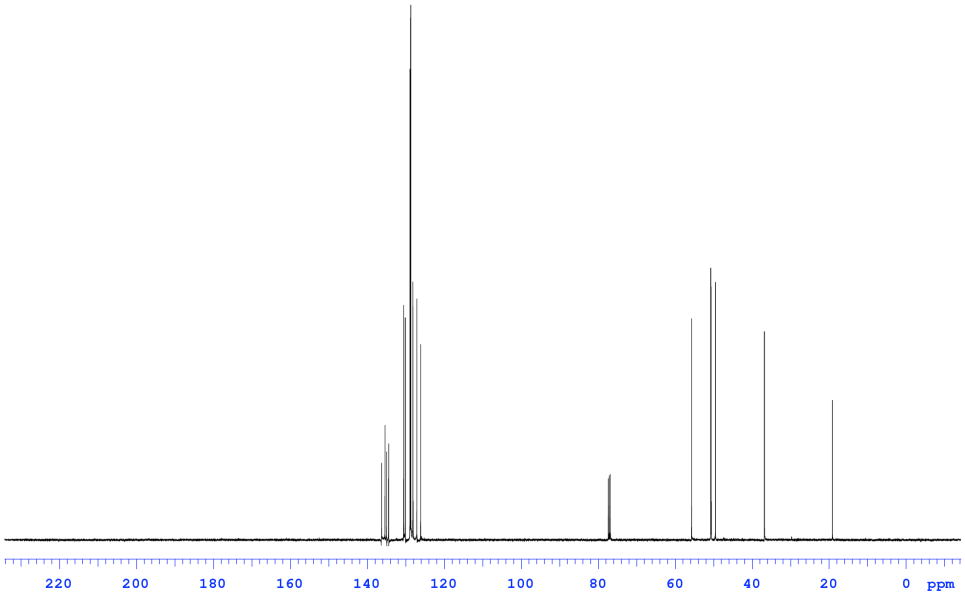
1.00
1.01
1.00
1.021.00
2.93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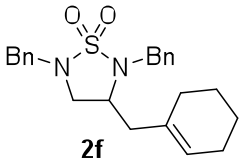
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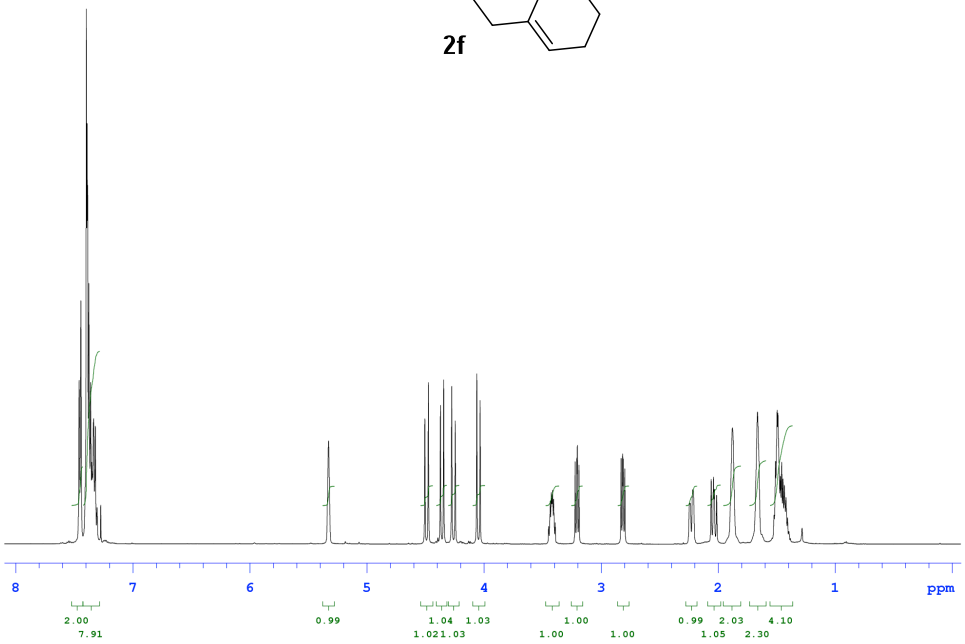
S
Bn
N
N
Bn

2f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6
5
4
3
2
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ppm
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7.91
0.99
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1.02
1.03
1.00
1.00
1.00
0.99
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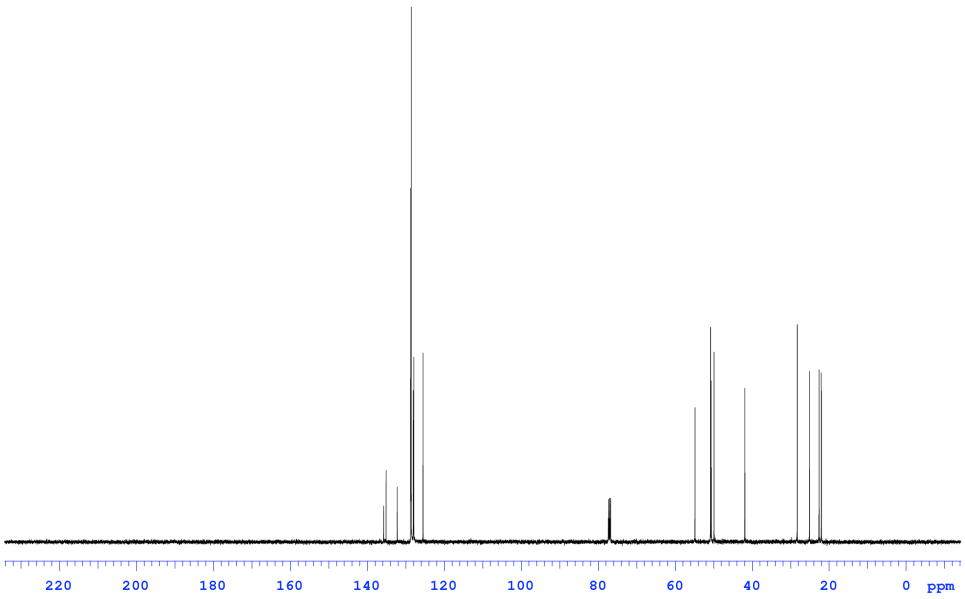
1.05
2.30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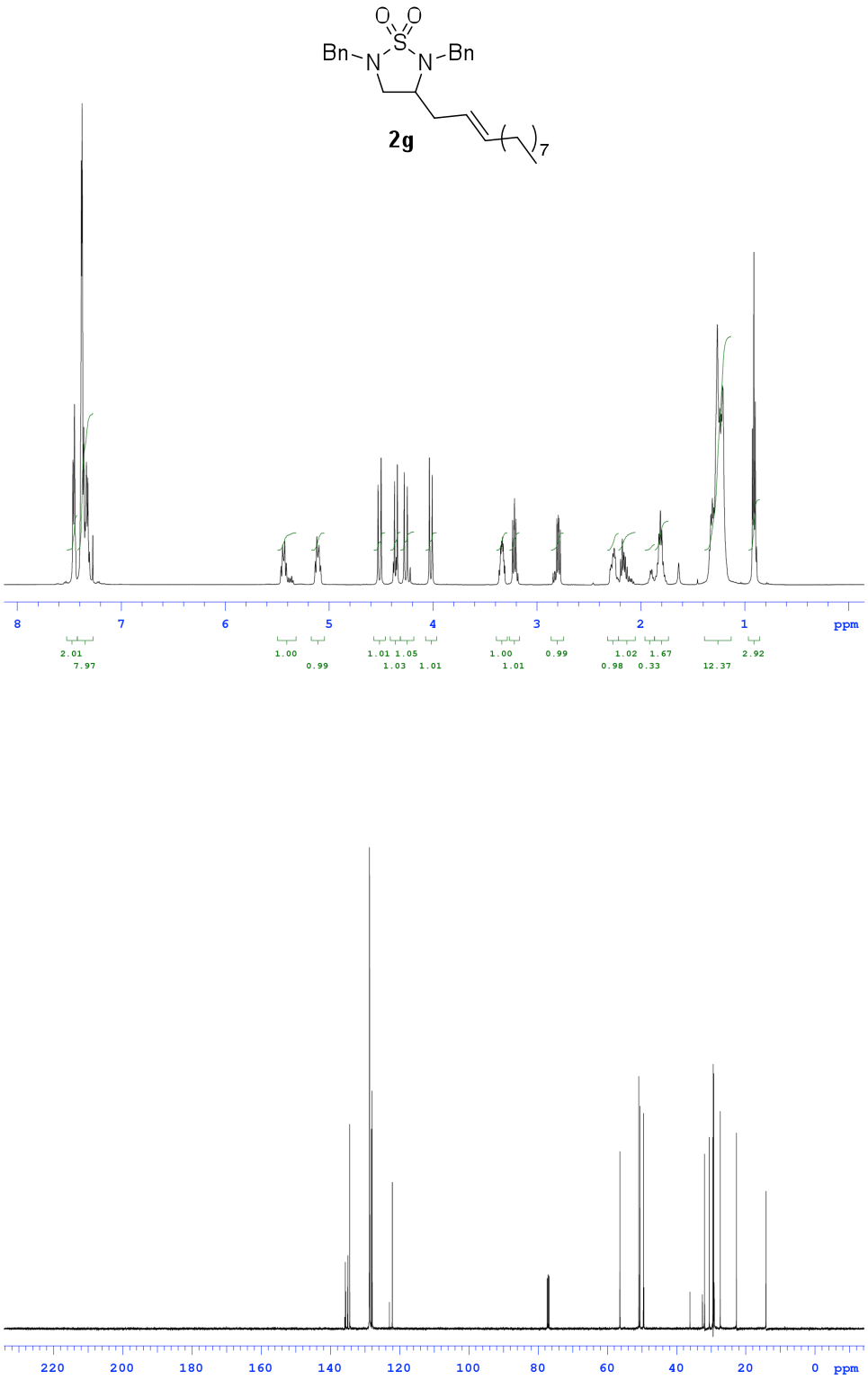
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O
O
N
Bn
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6
5
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3
2
1
ppm
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7.97
1.00
0.99
1.01
1.05
1.03
1.01
1.00
1.01
0.99
1.02
0.98
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120
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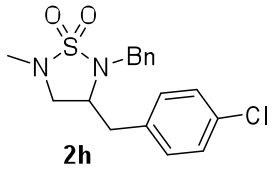
40
20
0
ppm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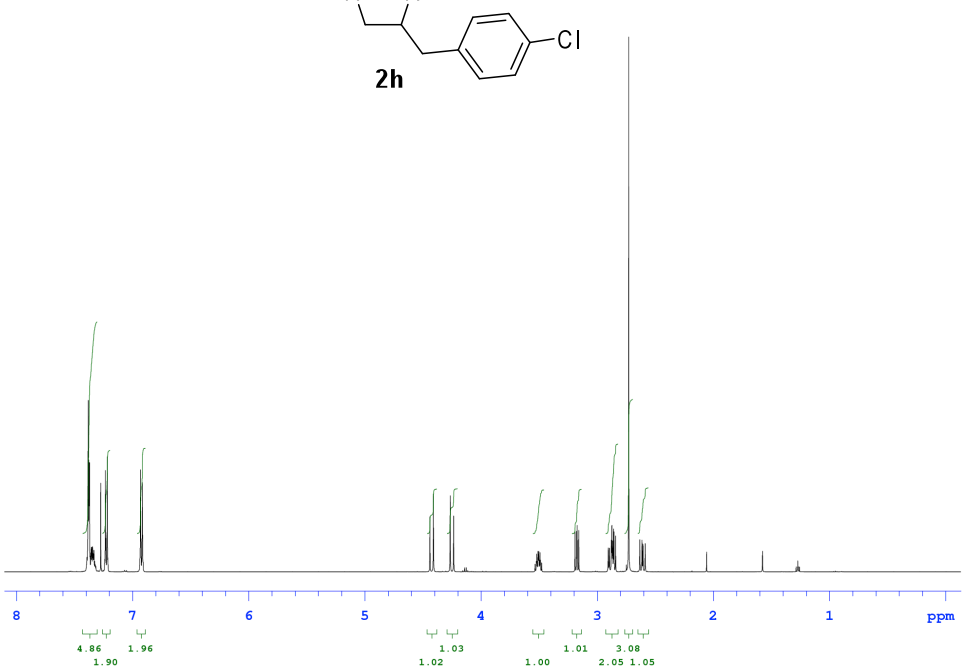
S
N
N
Bn
Cl

2h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5
4
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1.00
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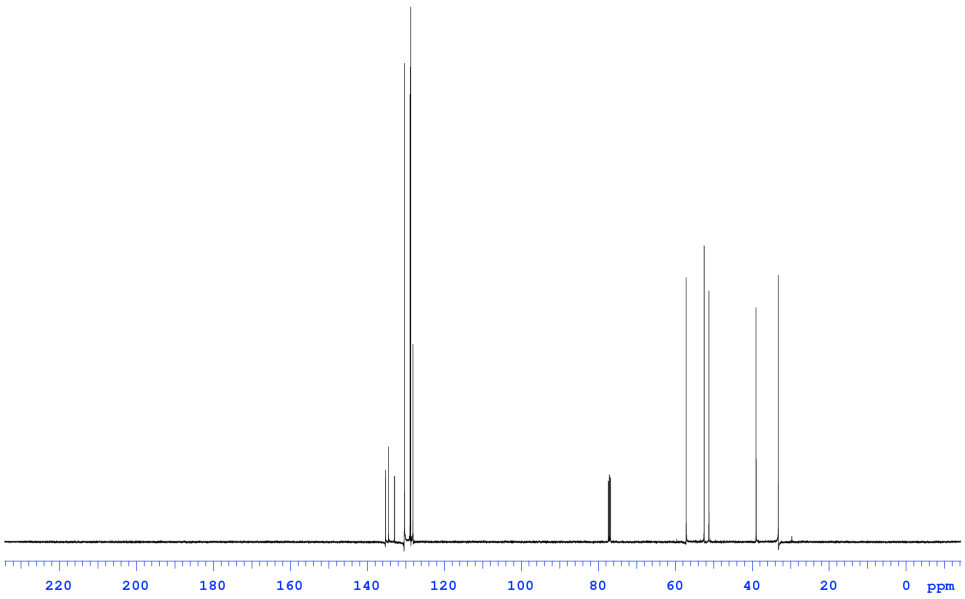
3.08
2.05
1.05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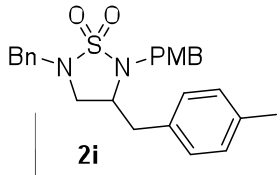
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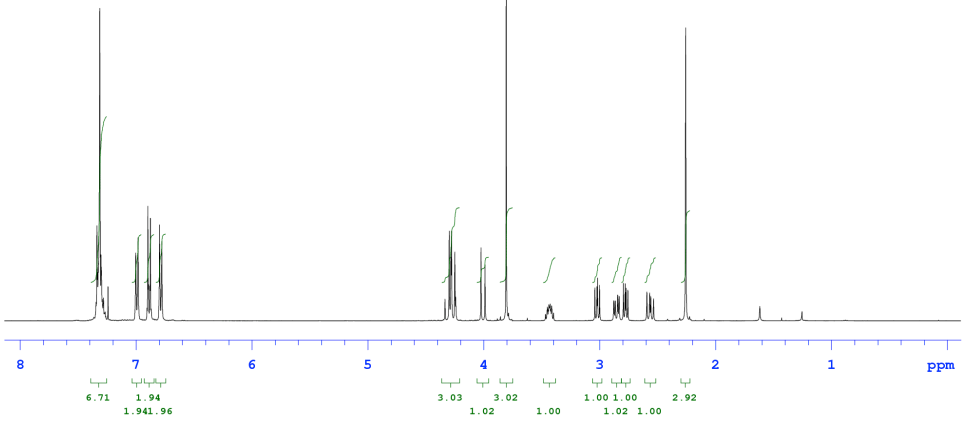
S
Bn
N
N
PMB

2i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6
5
4
3
2
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ppm
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3.03
3.02
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1.00
1.00
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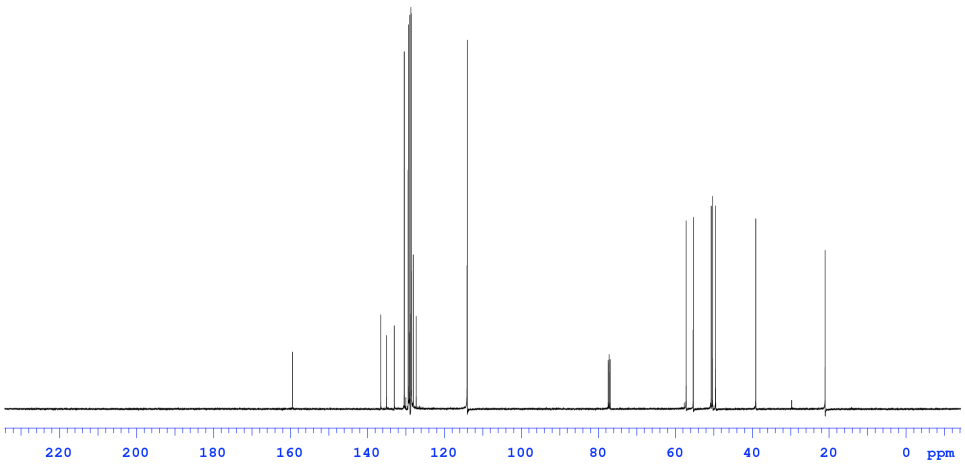
1.02
1.00
2.92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40
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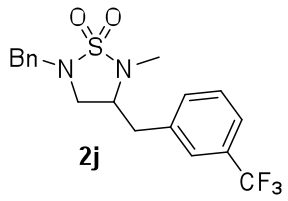
ppm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Bn
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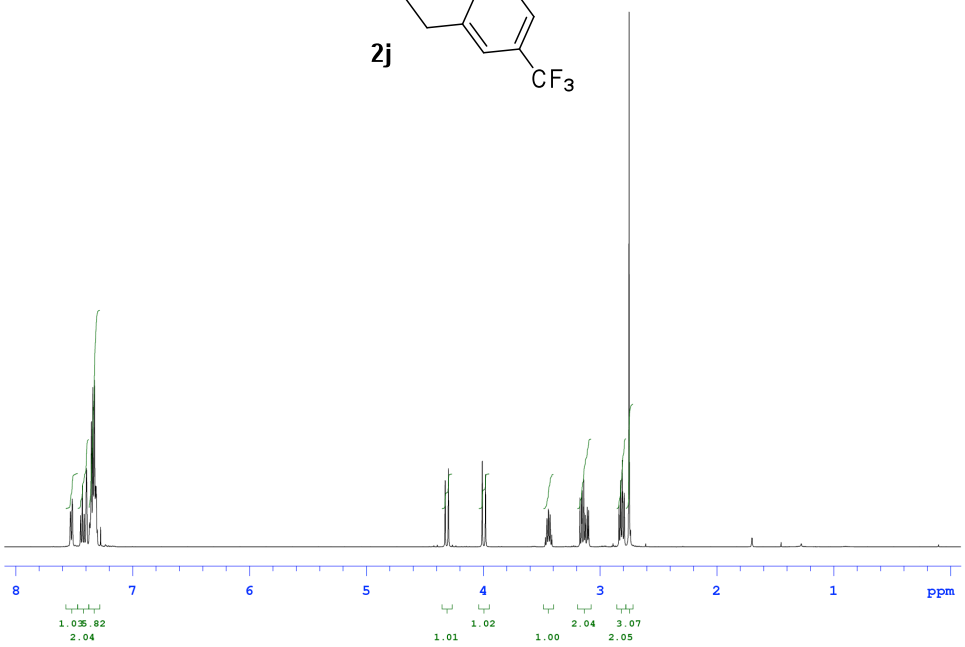
N
CF3

2j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6
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3
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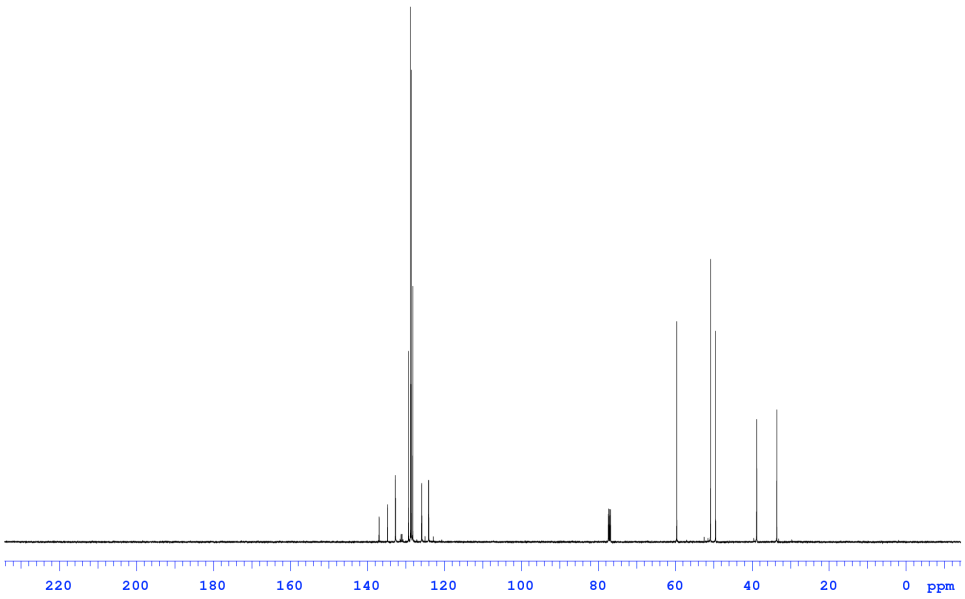
1.01
1.02
1.00
2.04
3.07
2.05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40
20
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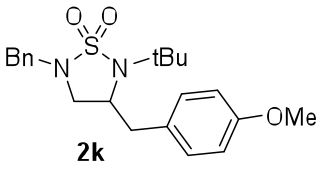
ppm


O
O
S
Bn
N
N
tBu
OMe

2k

8
7
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2
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ppm
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4.06
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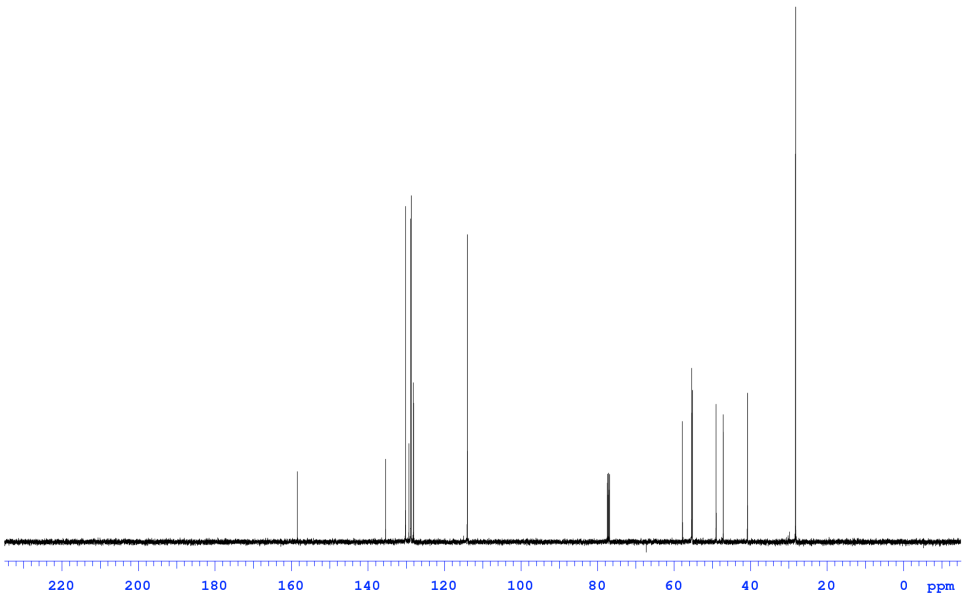
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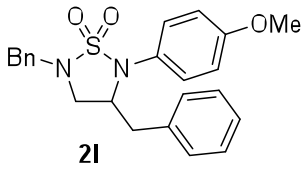
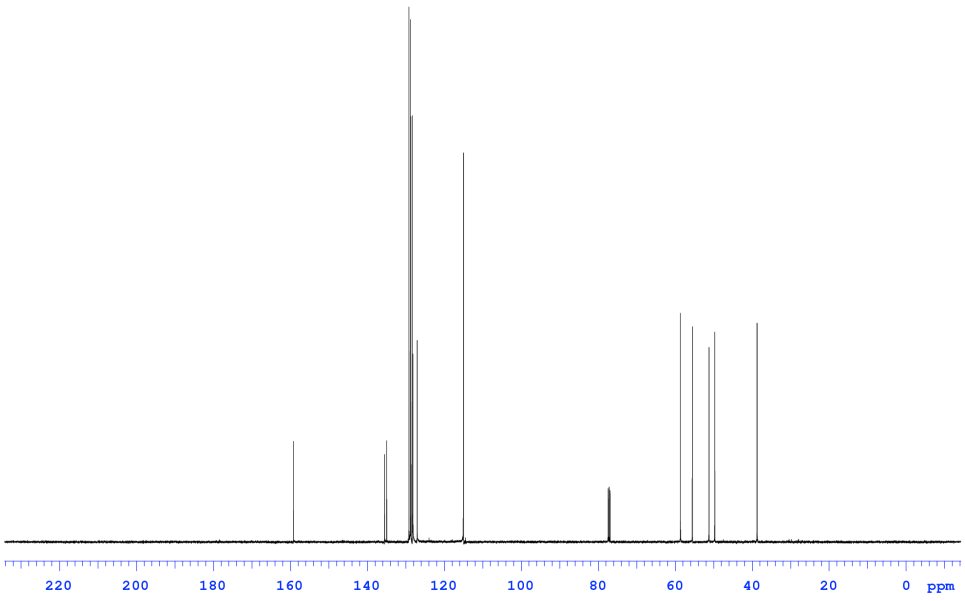
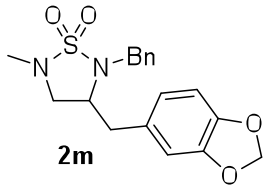

O
O
S
Bn
N
N
OMe

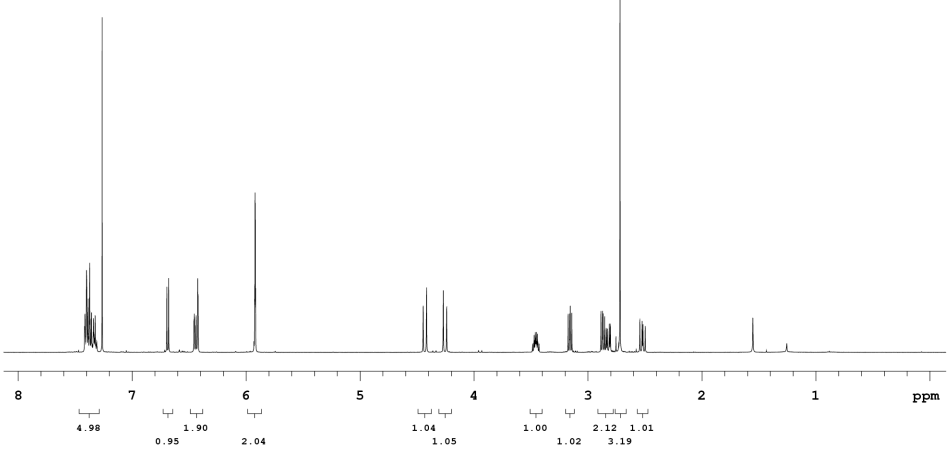
2l

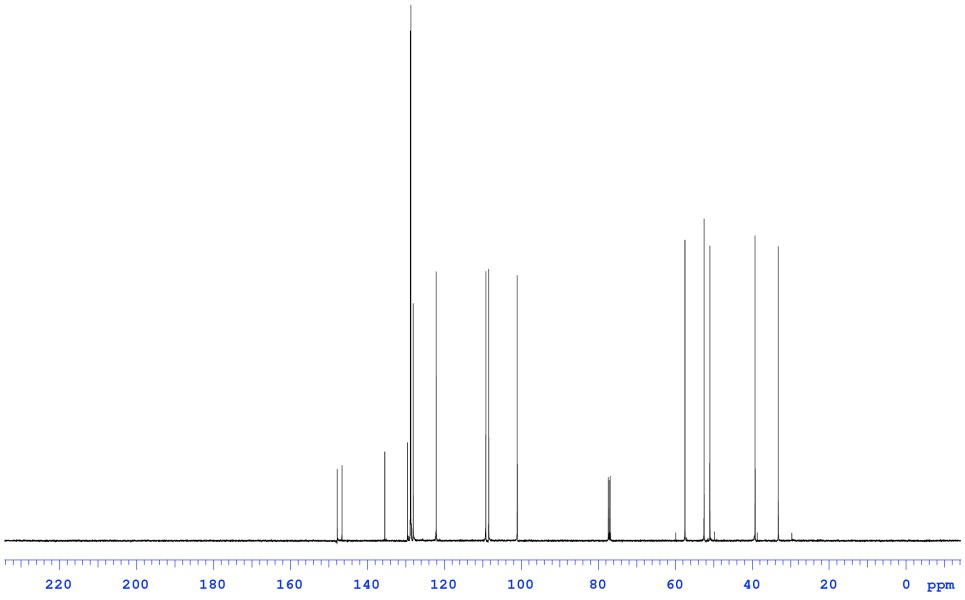
8
7
6
5
4
3
2
1
ppm
6.79
3.88
3.06
0.98
1.00
0.99
2.94
0.98
1.98
0.98

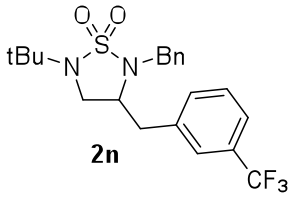

220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
N
Bn
O
O

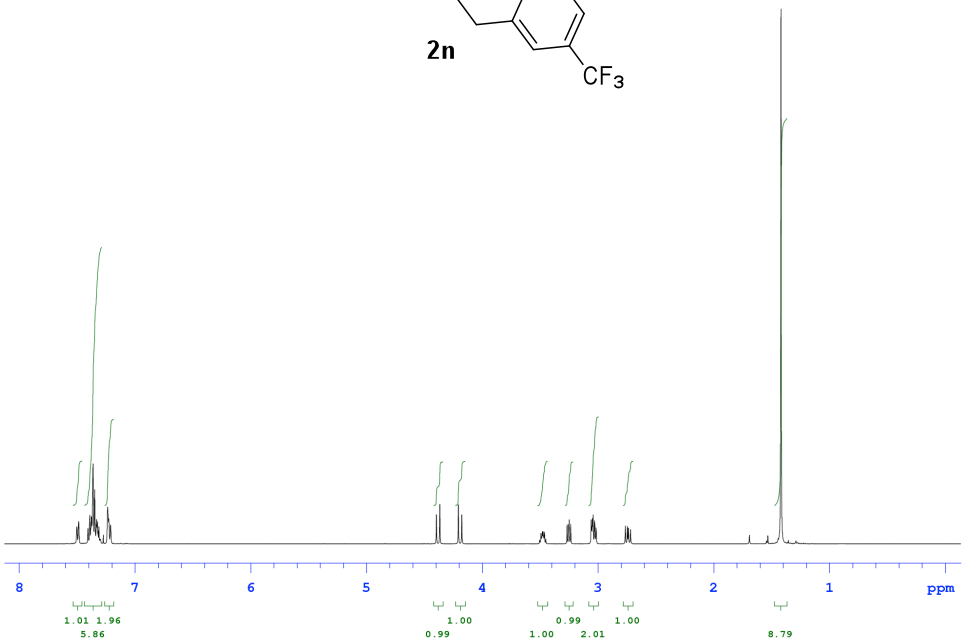
2m

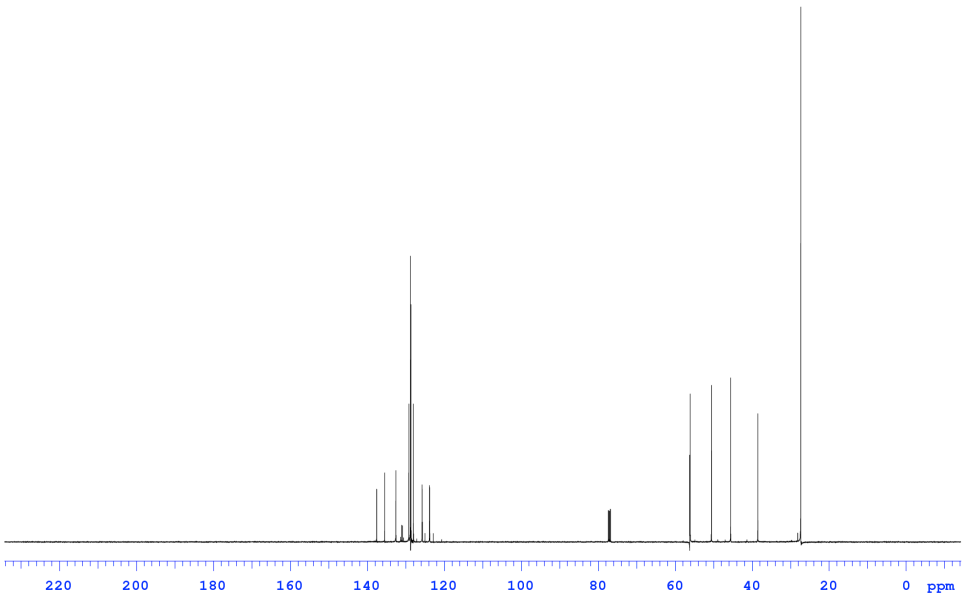

8
7
6
5
4
3
2
1
ppm
4.98
0.95
1.90
2.04
1.04
1.05
1.00
1.02
2.12
3.19
1.01

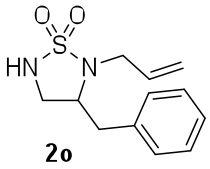

220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
tBu
N
N
Bn
CF3

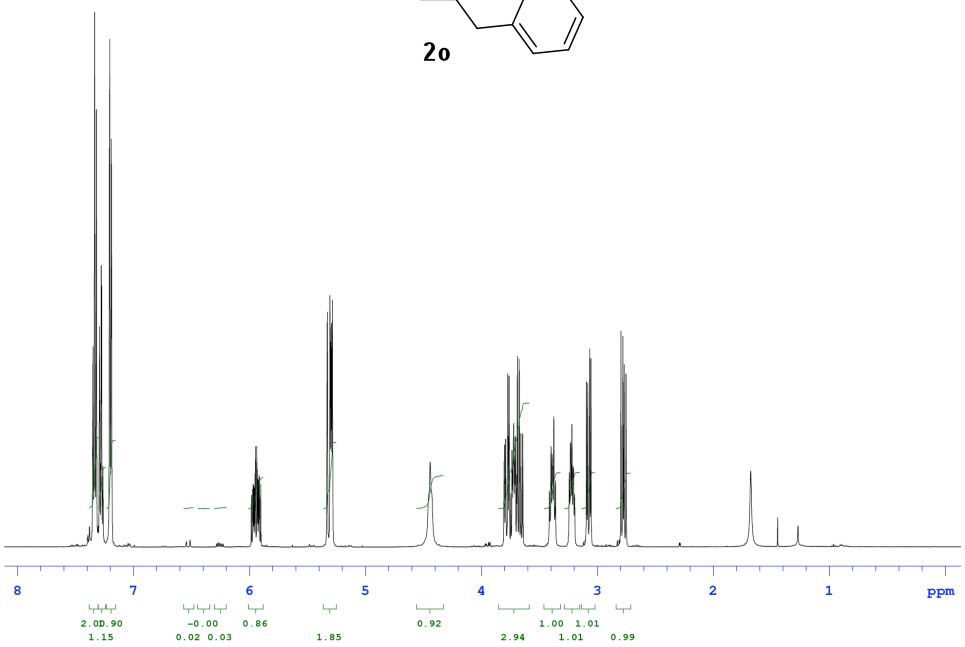
2n

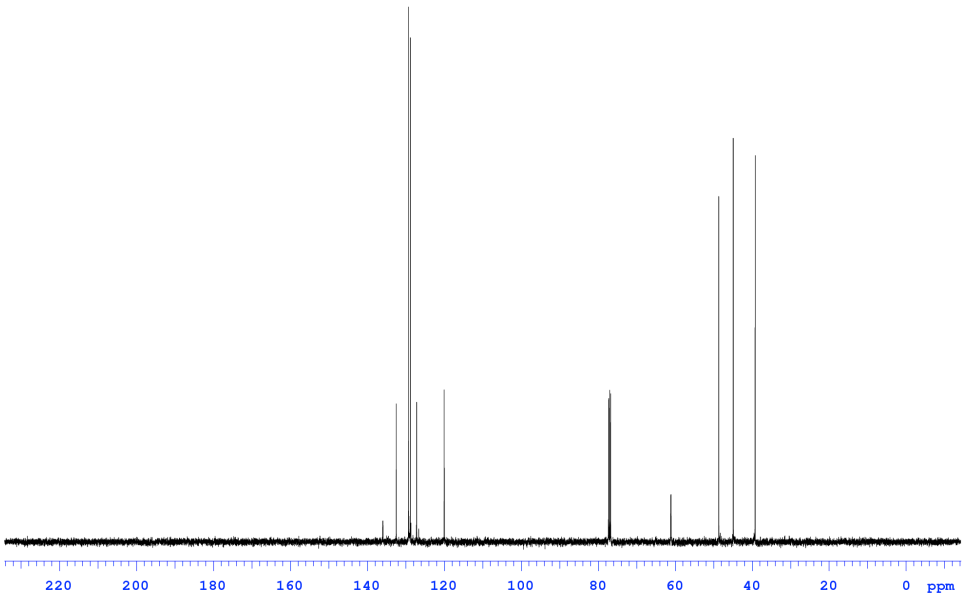

8
7
6
5
4
3
2
1
ppm
1.01 1.96
5.86
1.00
0.99
0.99
1.00
2.01
1.00
8.79

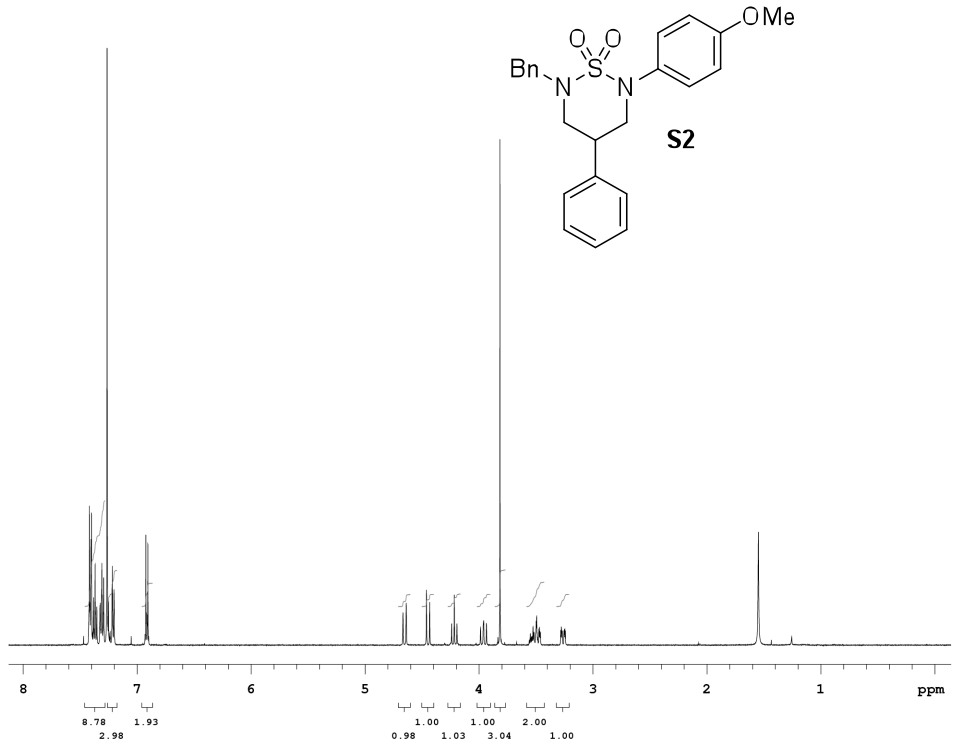

220
200
180
160
140
120
100
80
60
40
20
0
ppm

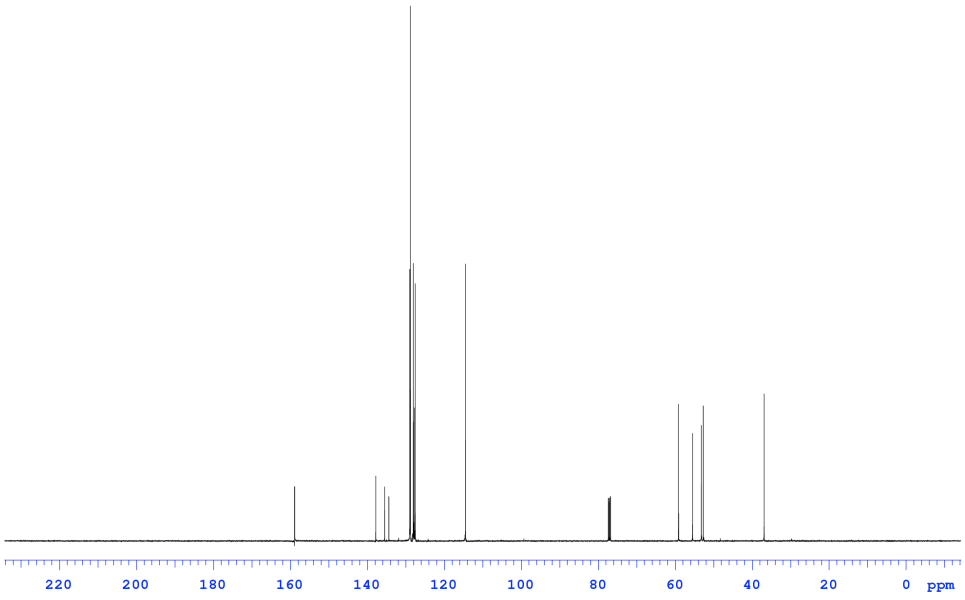

O
O
S
HN
N

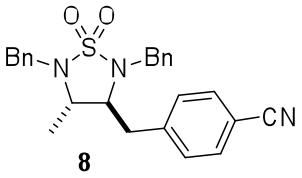
2o


8
7
6
5
4
3
2
1
ppm
2.00
0.90
1.15
0.02
0.03
0.86
1.85
0.92
2.94
1.00
1.01
1.01
0.99

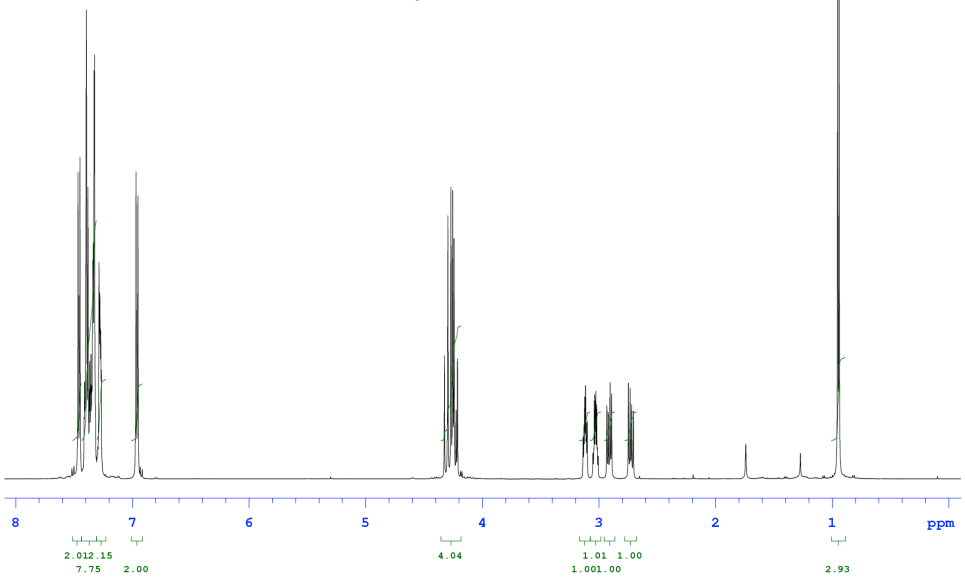

220
200
180
160
140
120
100
80
60
40
20
0
ppm

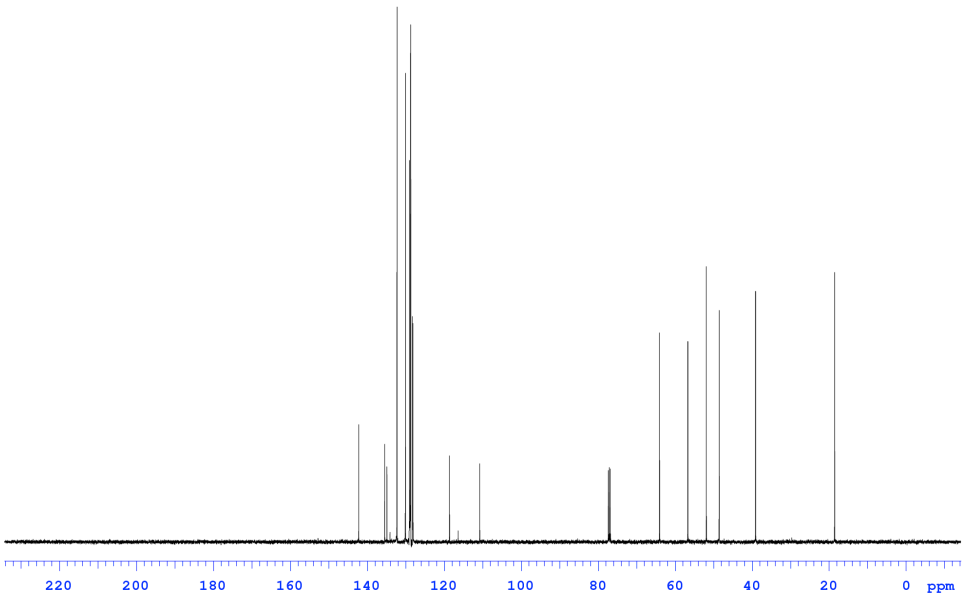

OMe
O
O
Bn
N
S
N
S2
8
7
6
5
4
3
2
1
ppm
8.78
2.98
1.93
0.98
1.00
1.03
1.00
3.04
2.00
1.00

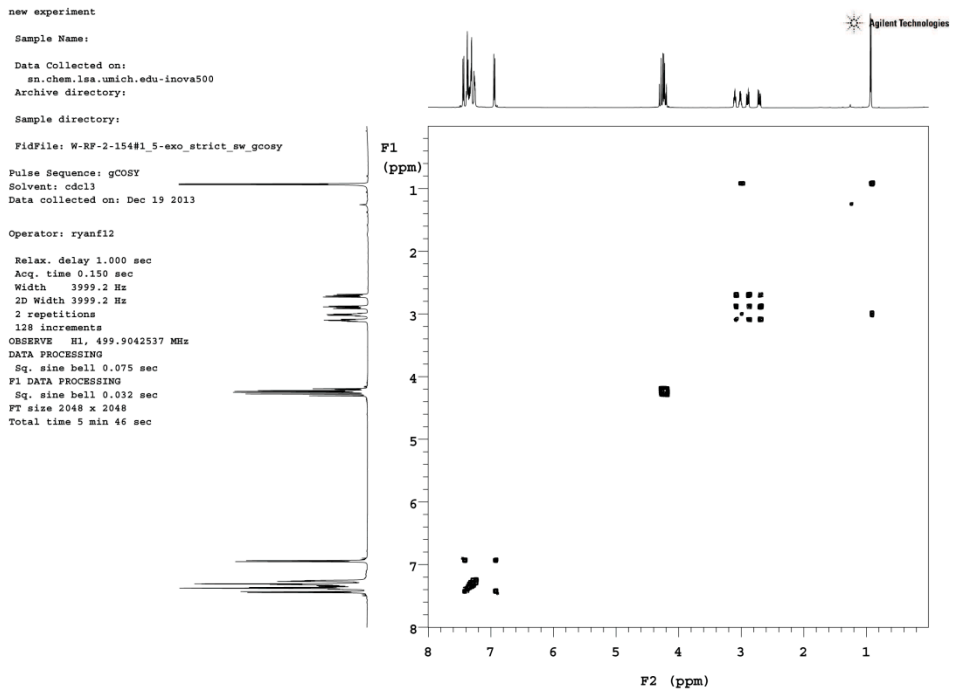

220
200
180
160
140
120
100
80
60
40
20
0
ppm

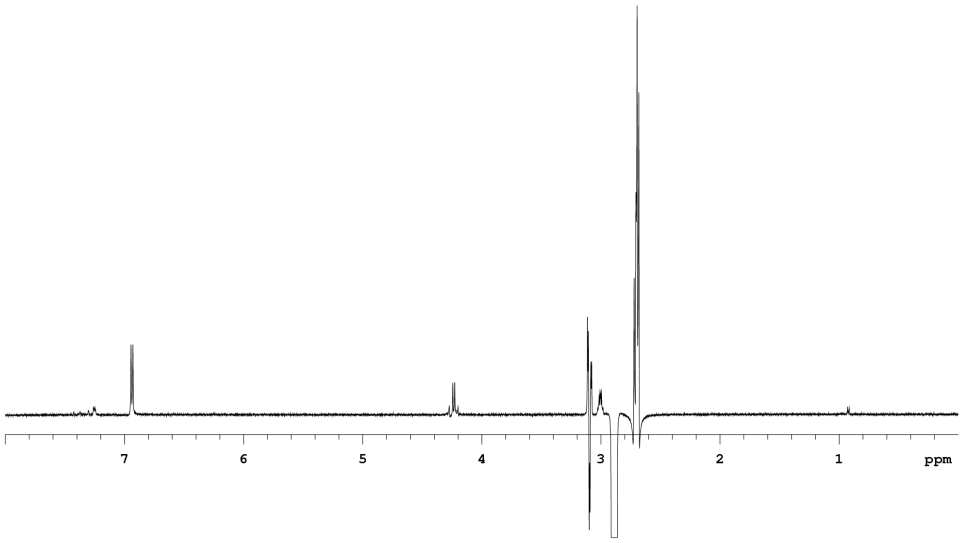

O
O
S
Bn
N
N
Bn
CN

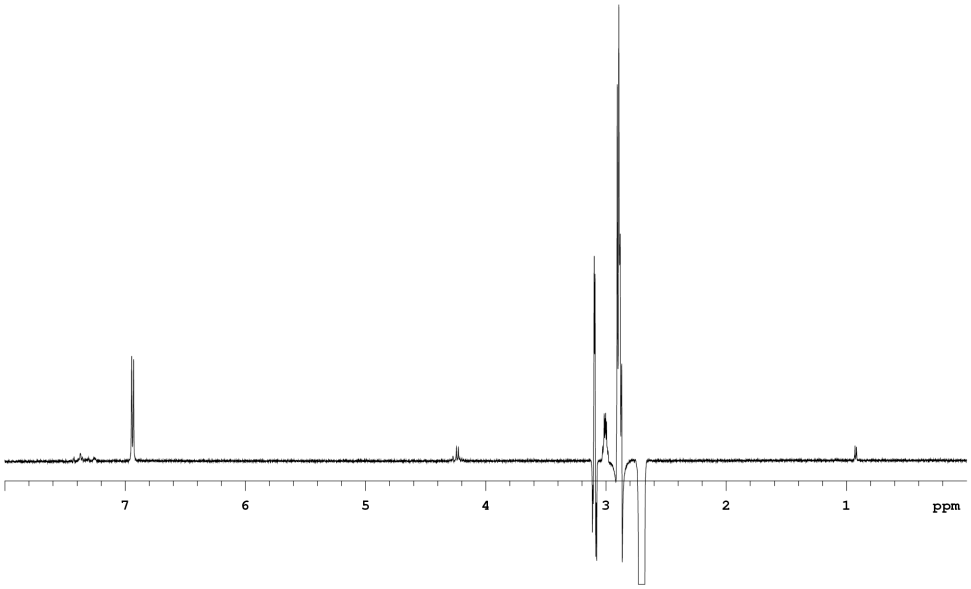
8

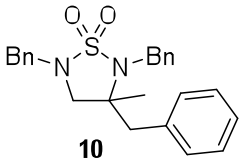

8
7
6
5
4
3
2
1
ppm
2.012.15
7.75
2.00
4.04
1.01
1.00
1.001.00
2.93


220
200
180
160
140
120
100
80
60
40
20
0
ppm

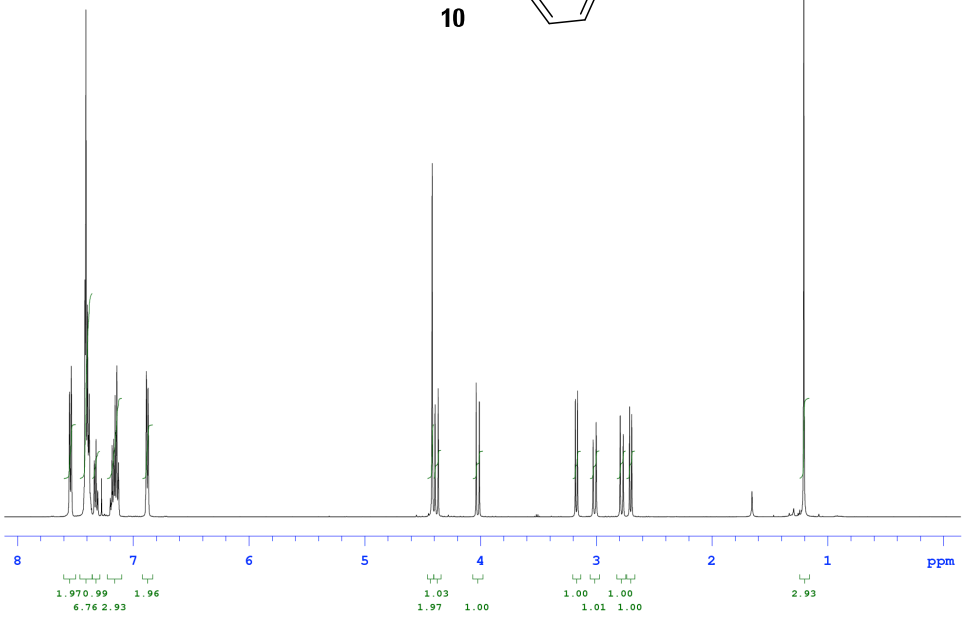

new experiment
Sample Name:
Data Collected on:
sn.chem.lsa.umich.edu-inova500
Archive directory:
Sample directory:
FidFile: W-RF-2-154#1_5-exo_strict_sw_gcosy
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Dec 19 2013
Operator: ryanf12
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3999.2 Hz
2D Width 3999.2 Hz
2 repetitions
128 increments
OBSERVE H1, 499.9042537 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.032 sec
FT size 2048 x 2048
Total time 5 min 46 sec
Agilent Technologies
F1 (ppm)
F2 (ppm)

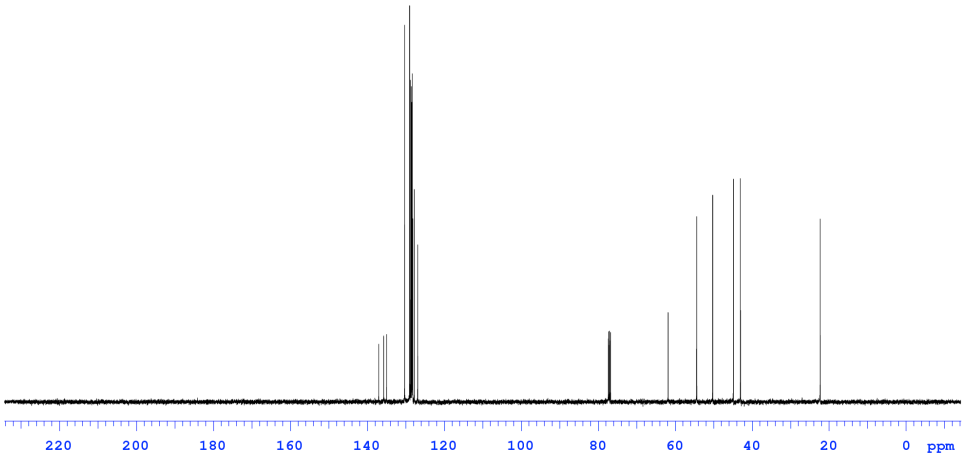

ppm

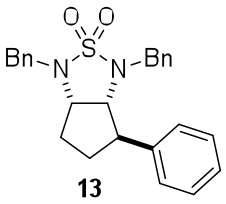

7
6
5
4
3
2
1
ppm


O
O
S
Bn
N
N
Bn

10

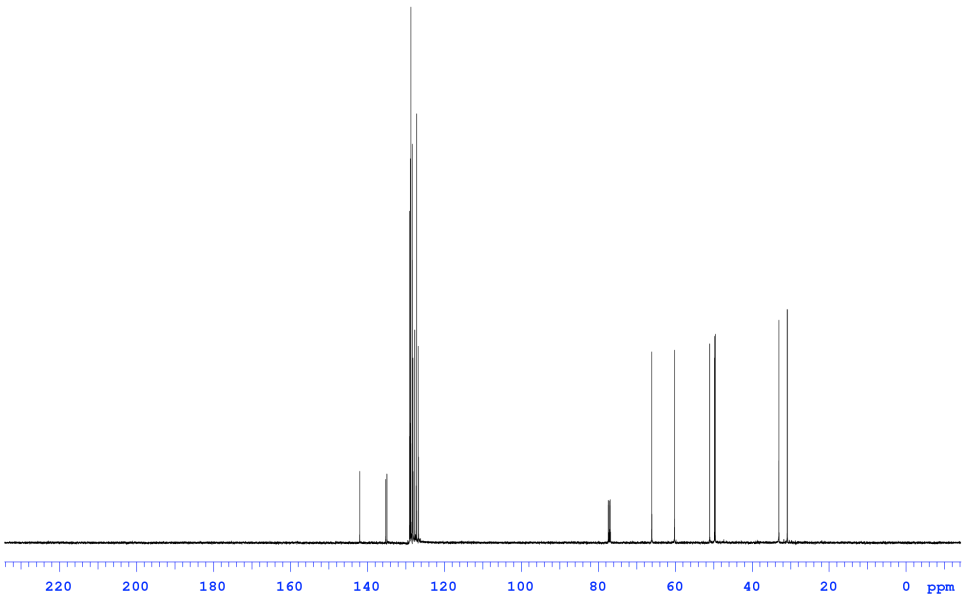

8
7
6
5
4
3
2
1
ppm
1.97 0.99
6.76 2.93
1.96
1.03
1.97
1.00
1.00
1.01
1.00
1.00
2.93

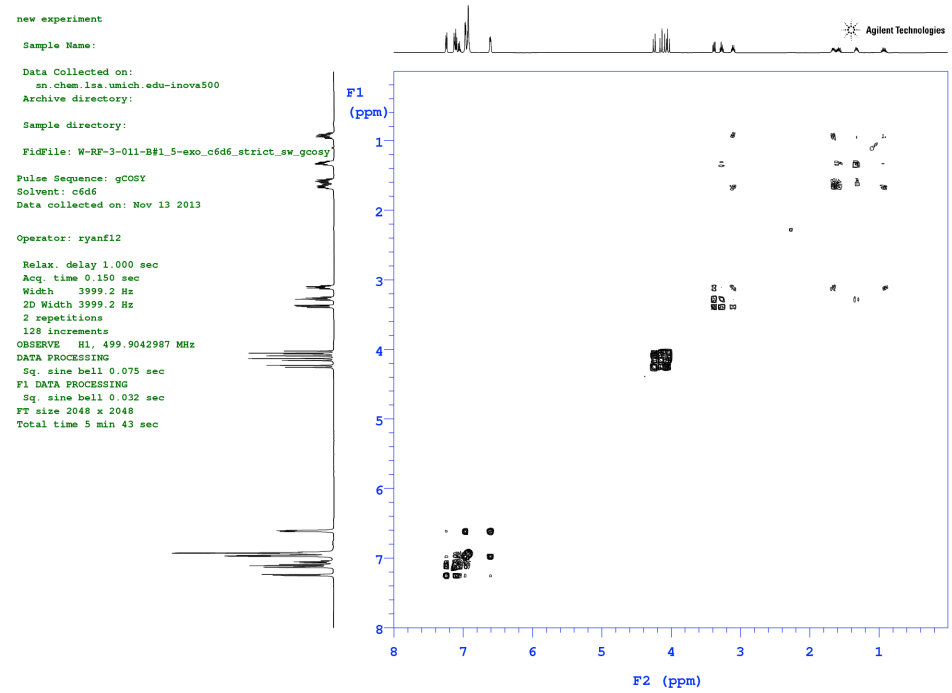

220
200
180
160
140
120
100
80
60
40
20
0
ppm

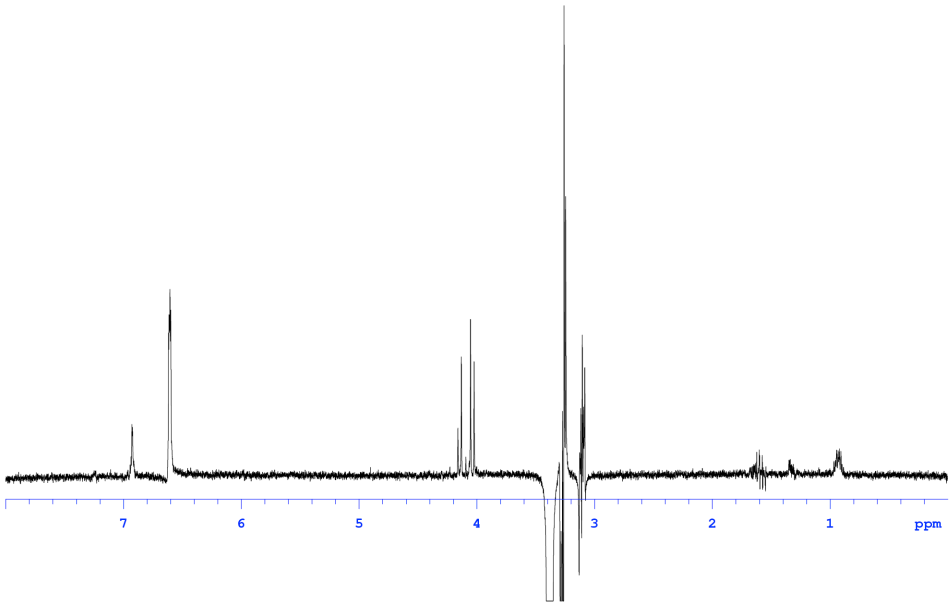

O
O
S
Bn
N
N
Bn

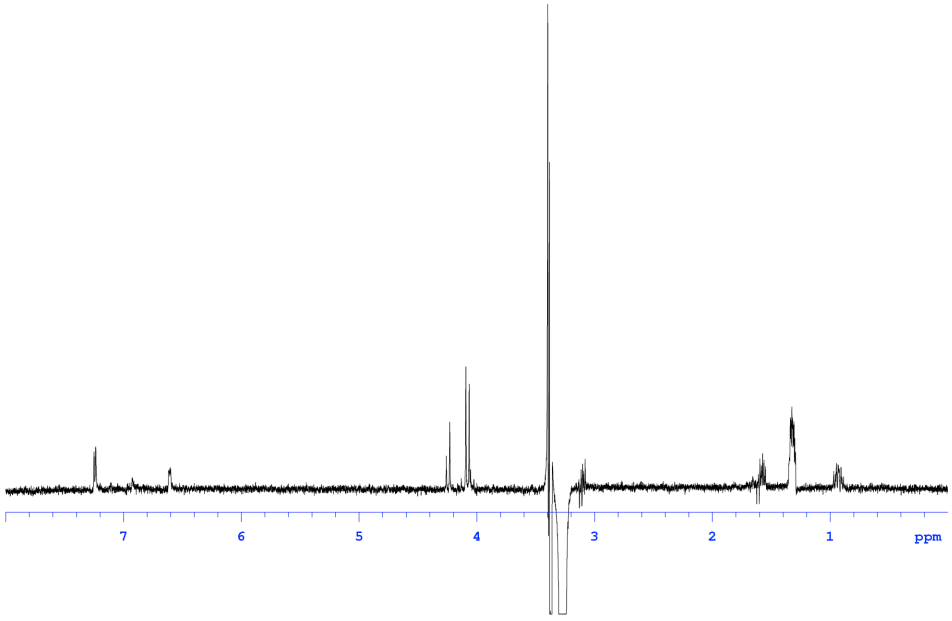
13

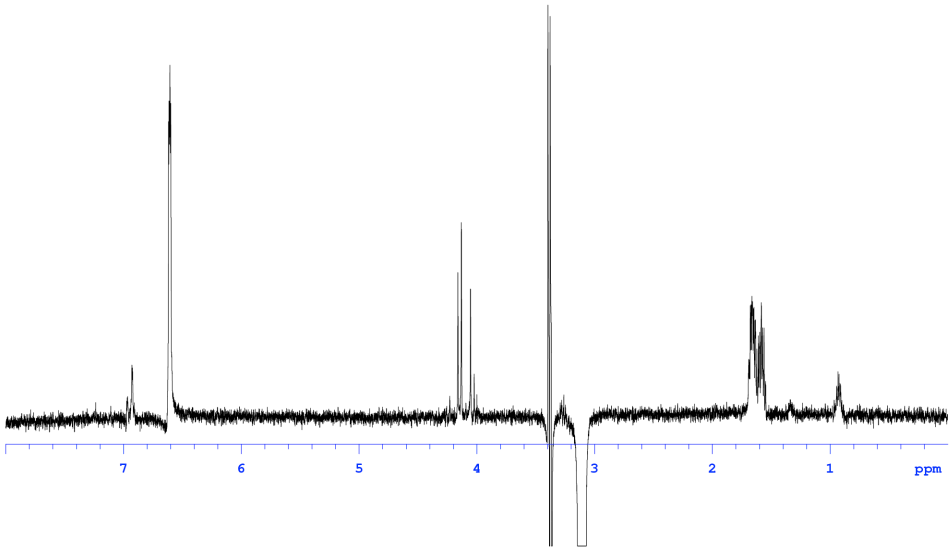
7
6
5
4
3
2
1
ppm
1.67
6.95
3.64
1.88
1.042.02
1.04
1.01
1.02
1.00
2.01
1.07
0.95

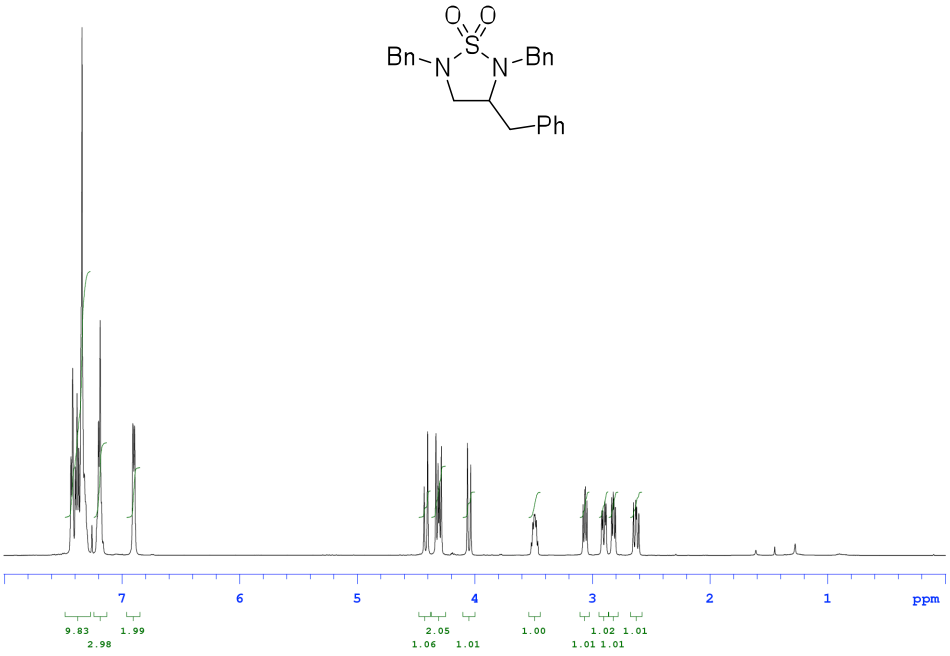

220
200
180
160
140
120
100
80
60
40
20
0
ppm

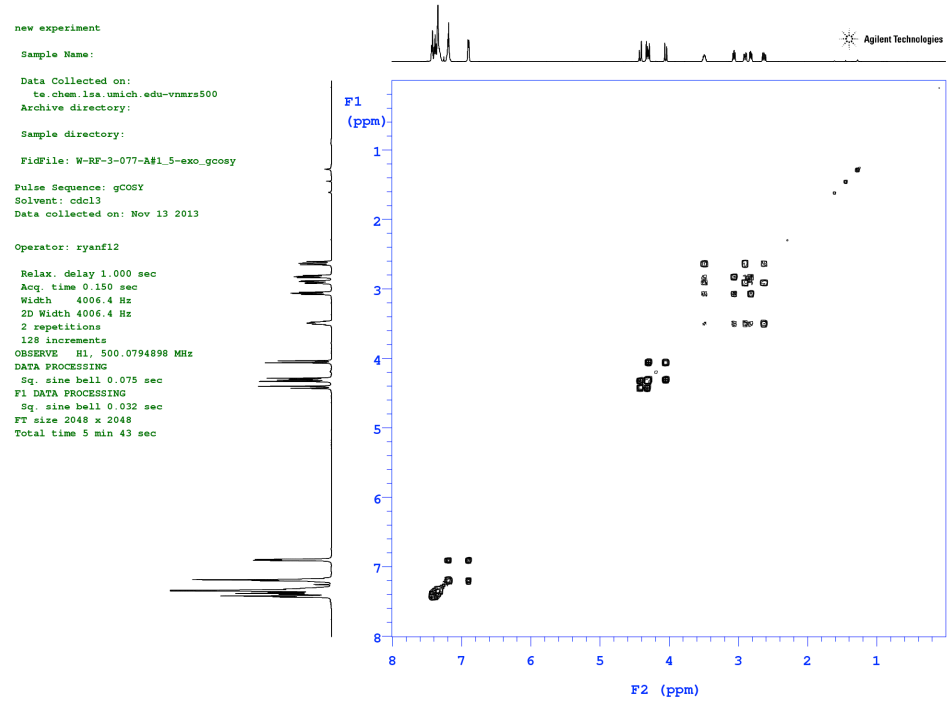

new experiment
Sample Name:
Data Collected on:
sn.chem.lsa.umich.edu-inova500
Archive directory:
Sample directory:
FidFile: W-RF-3-011-B#1_5-exo_c6d6_strict_sw_gcosy
Pulse Sequence: gCOSY
Solvent: c6d6
Data collected on: Nov 13 2013
Operator: ryanf12
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3999.2 Hz
2D Width 3999.2 Hz
2 repetitions
128 increments
OBSERVE H1, 499.9042987 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.032 sec
FT size 2048 x 2048
Total time 5 min 43 sec
Agilent Technologies
F1 (ppm)
F2 (ppm)

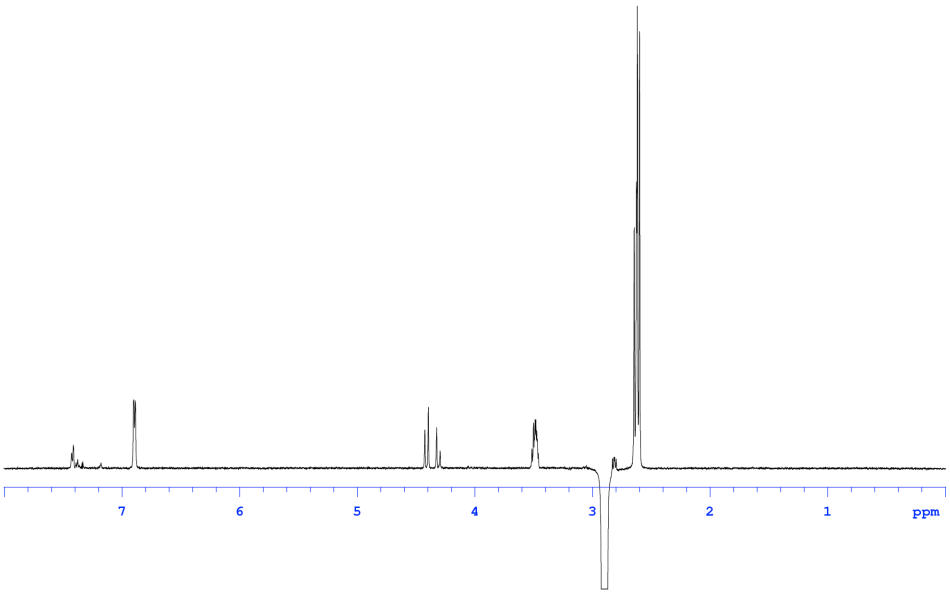

ppm

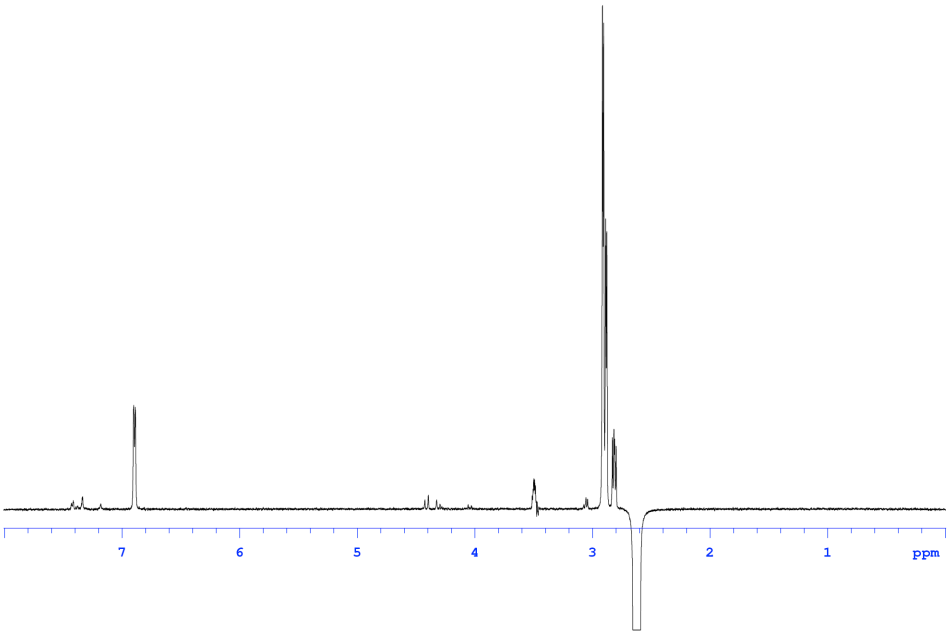

7
6
5
4
3
2
1
ppm

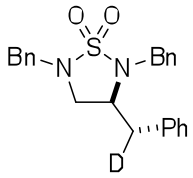

7
6
5
4
3
2
1
ppm


O
O
S
Bn
N
N
Bn
Ph
7
6
5
4
3
2
1
ppm
9.83
1.99
2.98
2.05
1.06
1.01
1.00
1.02
1.01
1.01
1.01

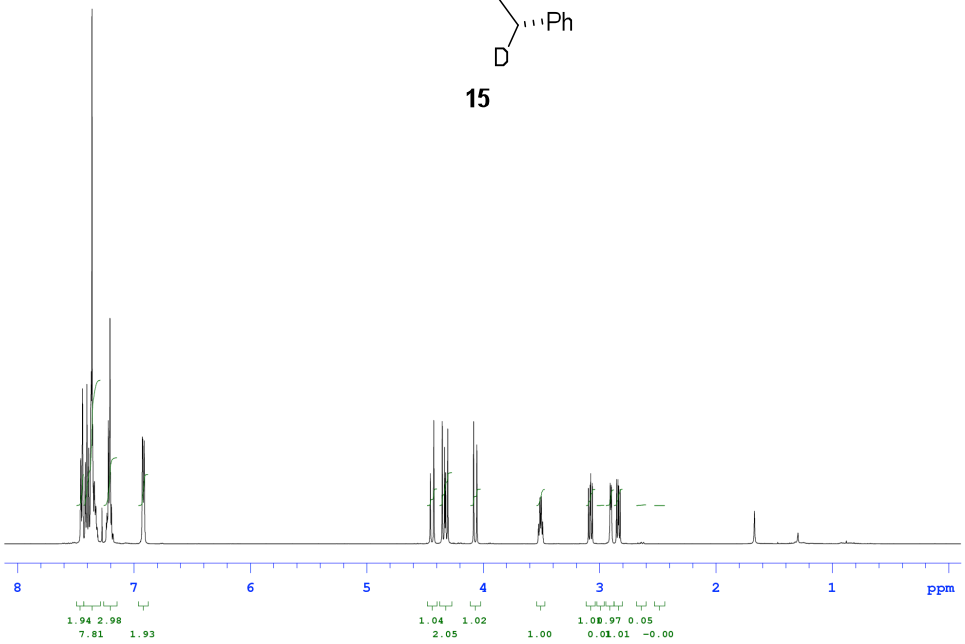

new experiment
Sample Name:
Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:
Sample directory:
FidFile: W-RF-3-077-A#1_5-exo_gcosy
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Nov 13 2013
Operator: ryanf12
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4006.4 Hz
2D Width 4006.4 Hz
2 repetitions
128 increments
OBSERVE H1, 500.0794898 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.032 sec
FT size 2048 x 2048
Total time 5 min 43 sec
Agilent Technologies
F1 (ppm)
F2 (ppm)

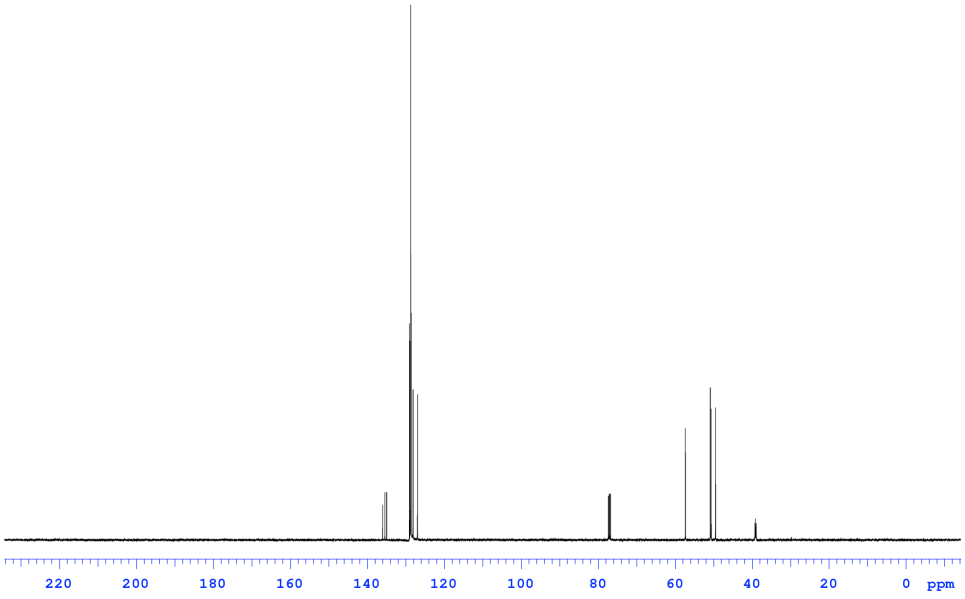

7
6
5
4
3
2
1
ppm

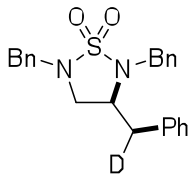

7
6
5
4
3
2
1
ppm


O
O
S
Bn
N
N
Bn
Ph
D

15

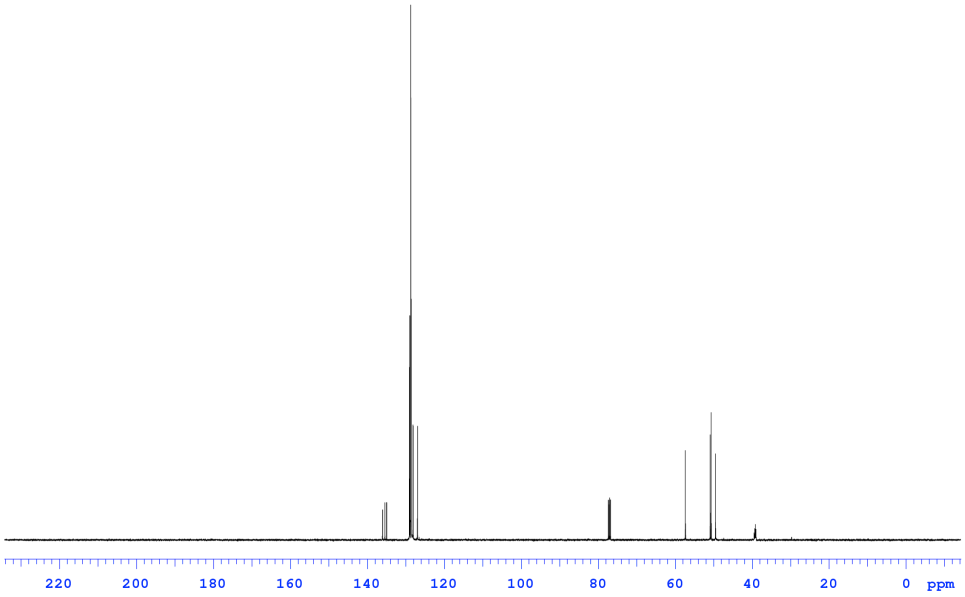

8
7
6
5
4
3
2
1
ppm
1.94 2.98
7.81 1.93
1.04 1.02
2.05
1.00
1.00 0.97 0.05
0.01 1.01 −0.00

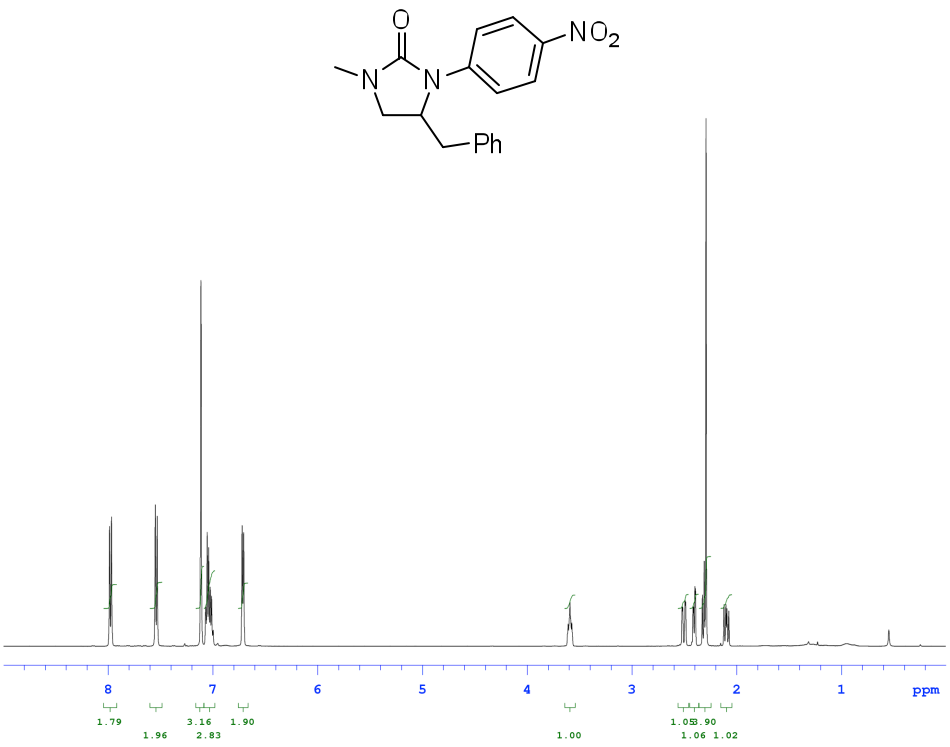

220
200
180
160
140
120
100
80
60
40
20
0
ppm

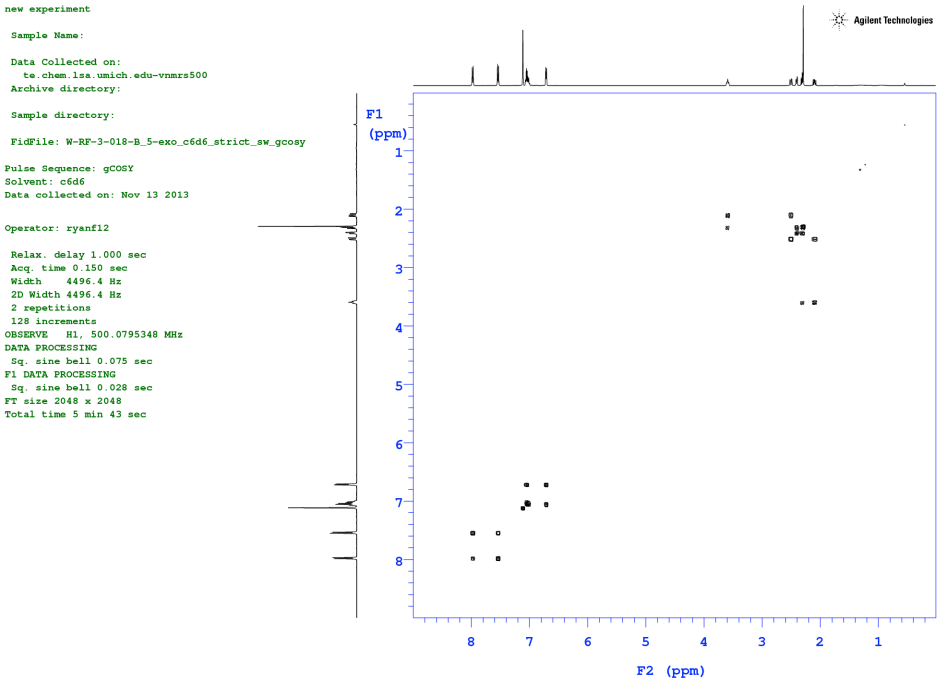

O
O
S
Bn
N
N
Bn
Ph
D

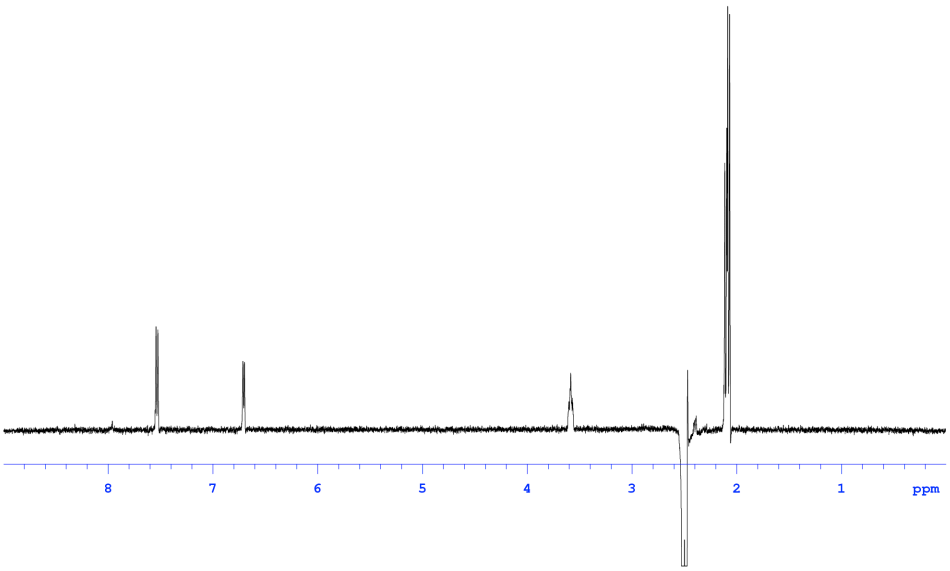
19

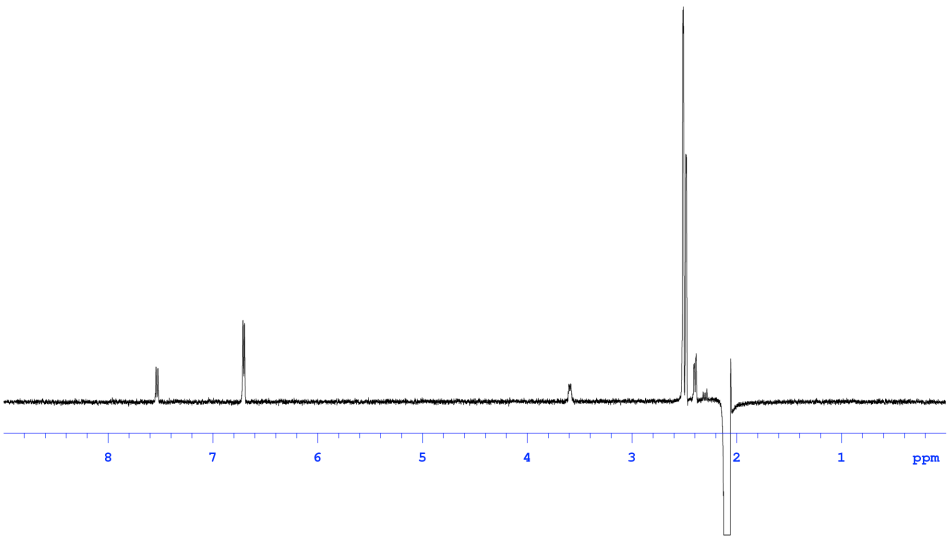
8
7
6
5
4
3
2
1
ppm
1.98 3.00
7.99 1.97
1.06 1.02
2.04
0.00 0.22 0.90
1.00 0.96 0.96 0.00

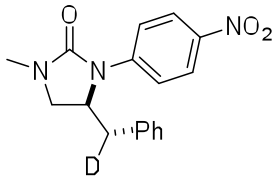

220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
N
N
NO2
Ph
8
7
6
5
4
3
2
1
ppm
1.79
1.96
3.16
2.83
1.90
1.00
1.05
1.06
3.90
1.02

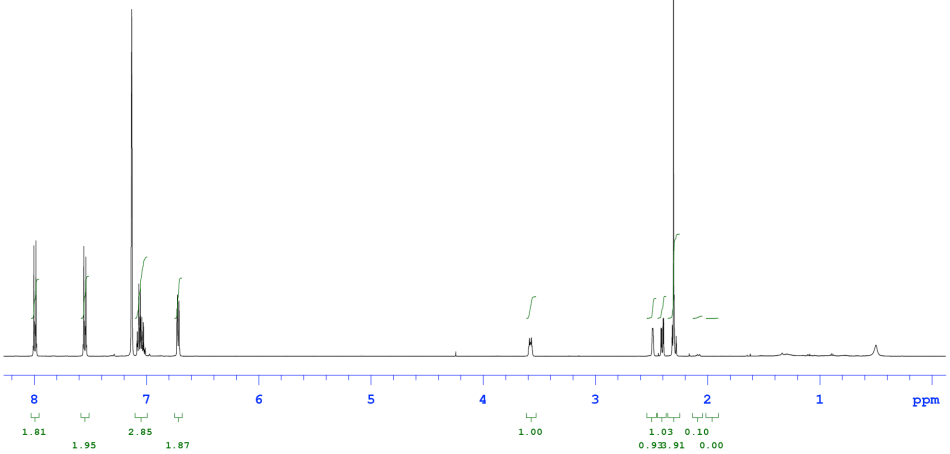

new experiment
Sample Name:
Data Collected on:
te.chem.lsa.umich.edu-vnmrs500
Archive directory:
Sample directory:
FidFile: W-RF-3-018-B_5-exo_c6d6_strict_sw_gcosy
Pulse Sequence: gCOSY
Solvent: c6d6
Data collected on: Nov 13 2013
Operator: ryanf12
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4496.4 Hz
2D Width 4496.4 Hz
2 repetitions
128 increments
OBSERVE H1, 500.0795348 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.028 sec
FT size 2048 x 2048
Total time 5 min 43 sec
Agilent Technologies
F1 (ppm)
F2 (ppm)


8
7
6
5
4
3
2
1
ppm


8
7
6
5
4
3
2
1
ppm


O
NO2
N
N
Ph
D

22


8
7
6
5
4
3
2
1
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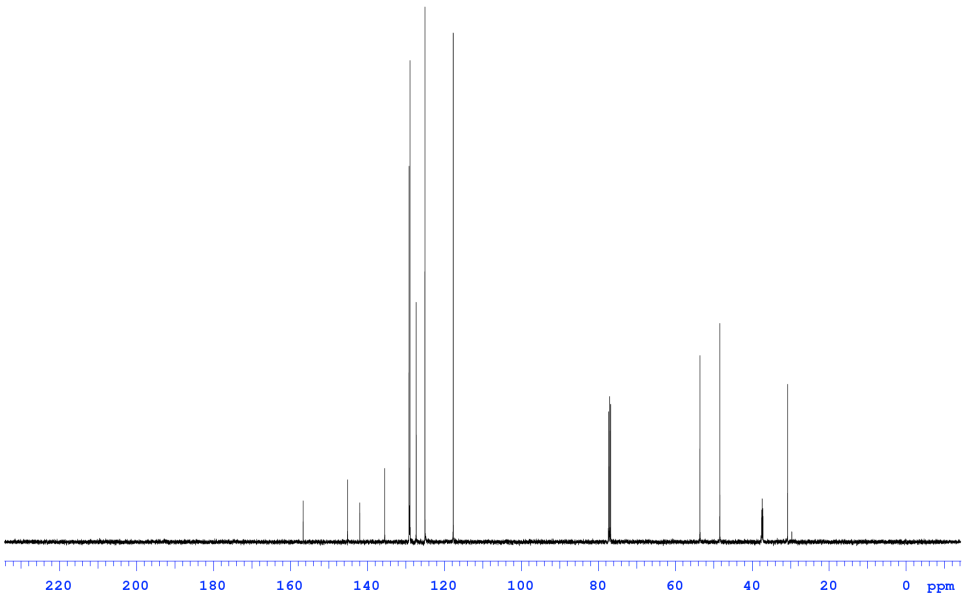
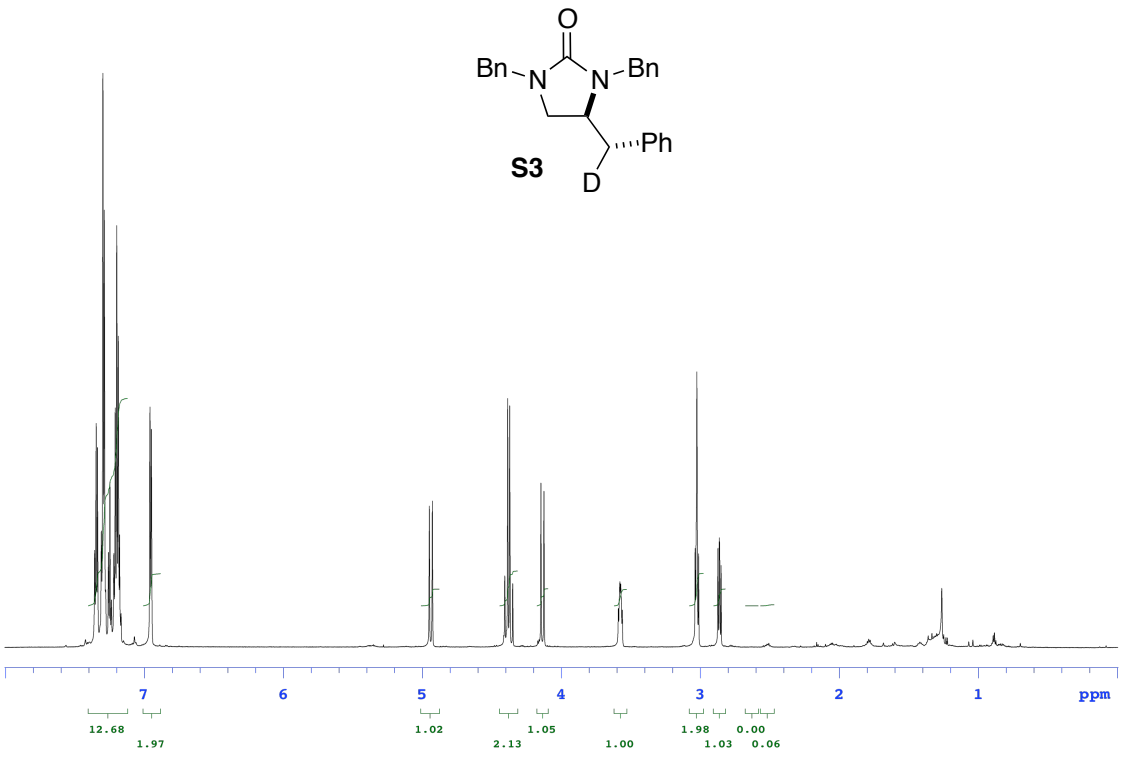
1.95
2.85
1.87
1.00
1.03
0.10
0.93
3.91
0.00


220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Bn
N
N
Bn
Ph
D
7
6
5
4
3
2
1
ppm
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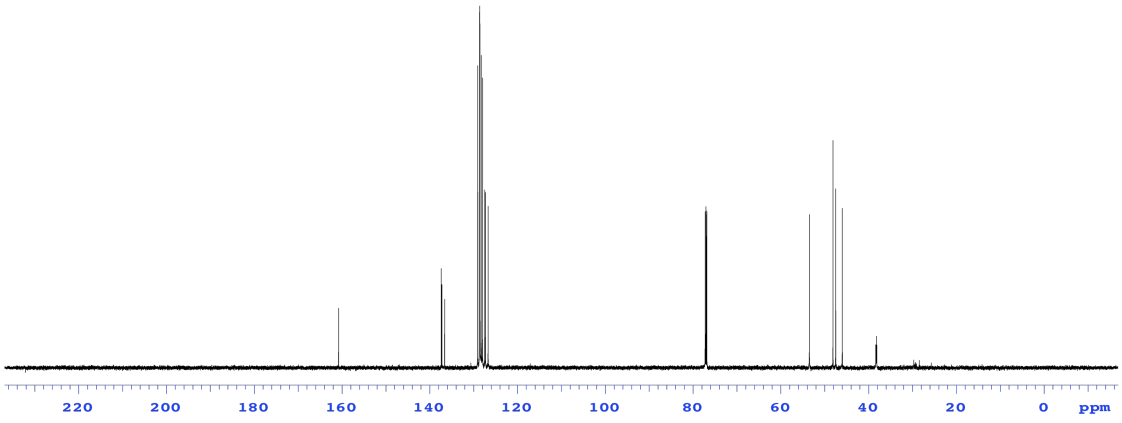
1.97
1.02
2.13
1.05
1.00
1.98
1.03
0.00
0.06

S3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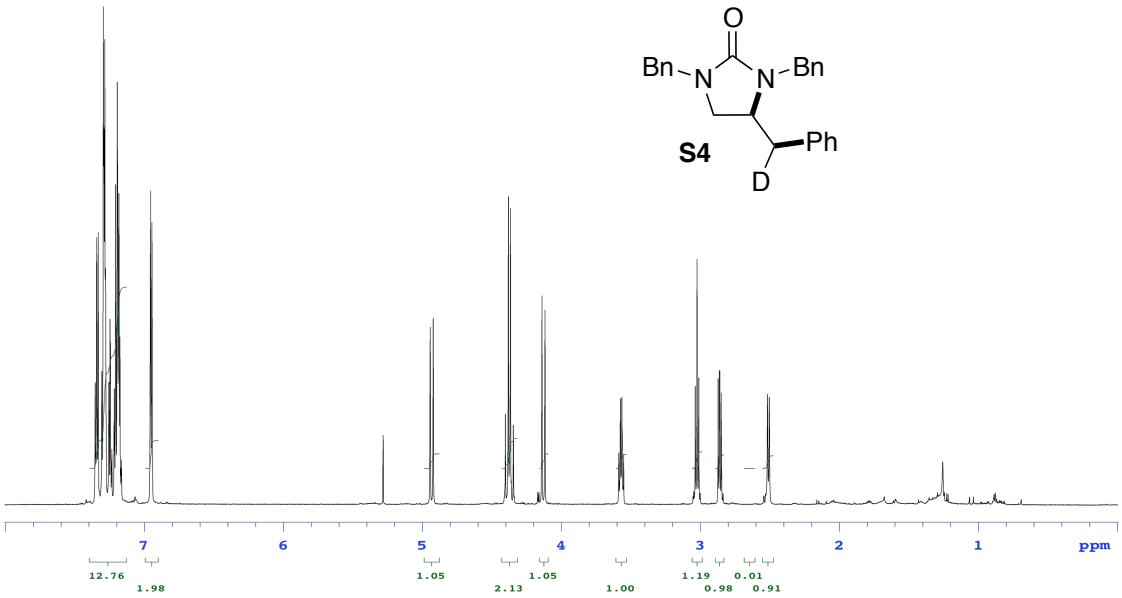
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Bn
N
N
Bn
Ph
D
S4
7
6
5
4
3
2
1
ppm
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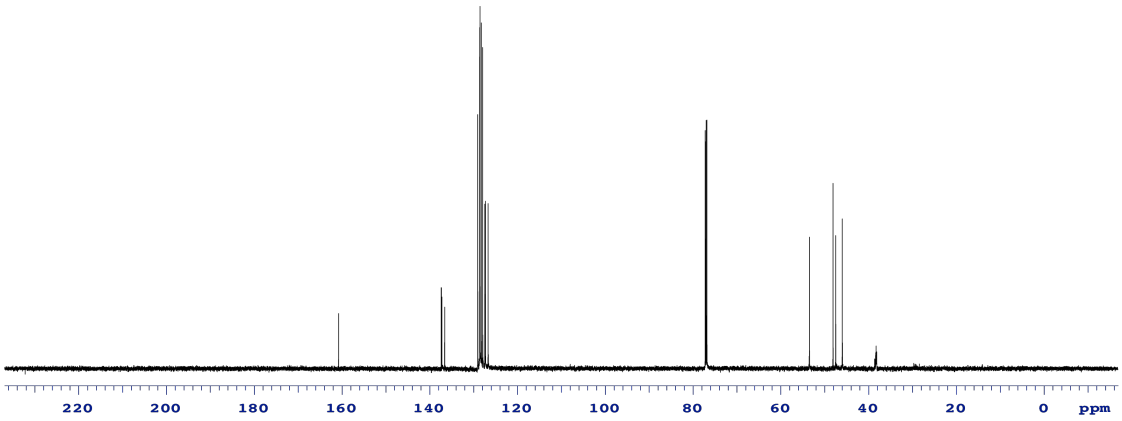
1.98
1.05
1.05
2.13
1.00
1.19
0.01
0.98
0.91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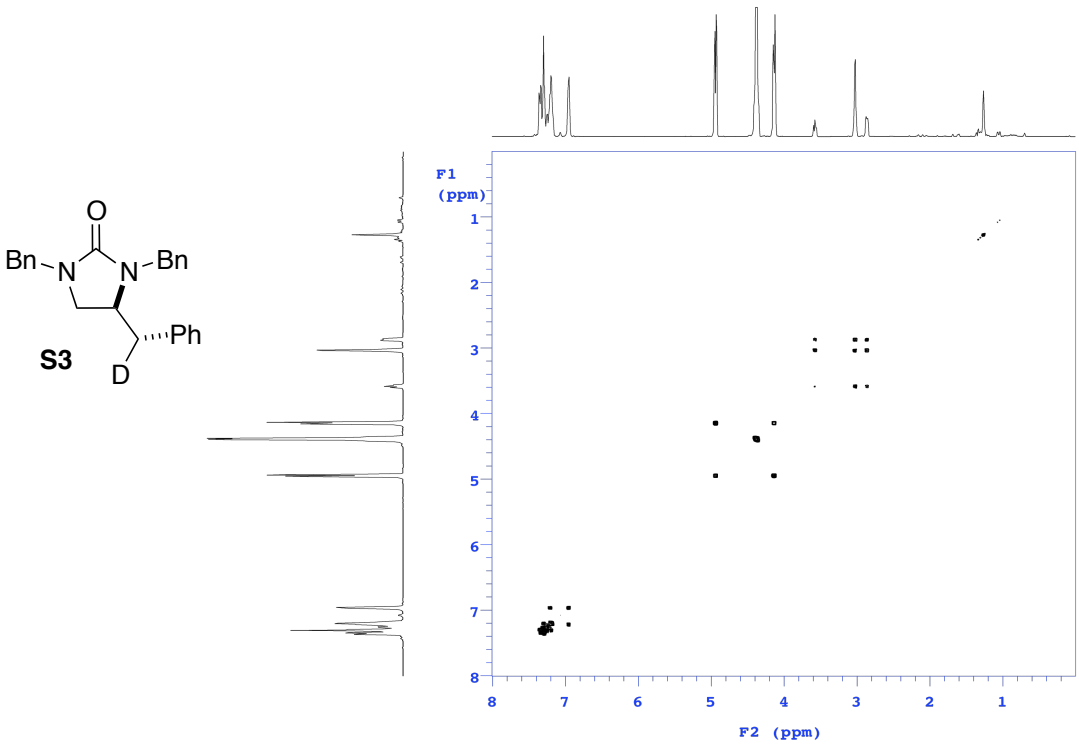
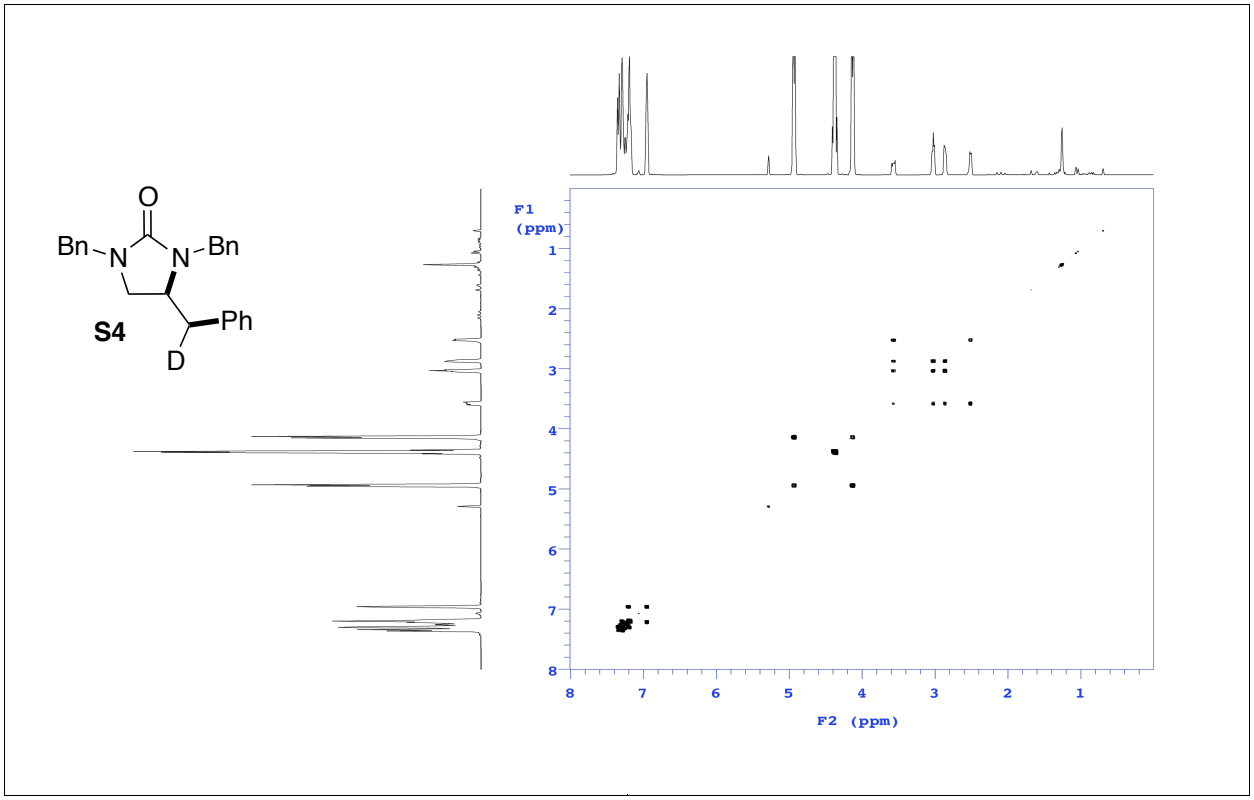
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Bn
N
N
Bn
Ph
D
S3
F1 (ppm)
F2 (ppm)


O
Bn
N
N
Bn
Ph
D
S4
F1 (ppm)
F2 (ppm)